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ANALYTICA CHIMICA ACTA VOL. 16 (1957)
AUTHOR INDEX

Andersson B., see Gabrielson, G.
Anson, F. C., see Lingane, J. J.
Artigas, J., see Buscaróns, F.
Athavale, V. T., see Nadkarni, M. N.
Badoz-Lambling, J. 285
Banerjee, G. 56, 62
Banick, Wm. M. and G. Frederick Smith 464
Bard, A. J., see Lingane, J. J.
Barltrop, J. A. and K. J. Morgan . . . 520
Basu, S. and K. K. Chatterjee 332
Belcher, R., A. M. G. MacDonald and E. Parry 524
Bjarke, G. O., see Colichman, E. L.
Blair, A. J. and D. A. Pantony . . . 121
Blake, G. G. 238
Blanquet, P. 44
Block, B. P., see Callahan, C. M.
Bobtelsky, M. and J. Eisenstadter . . 479
Bobtelsky, M. and R. Rafailoff . 321, 488
Bobtelsky, M. and I. Yulius 76
Bock, R. and T. Hoppe 406
Boot-Meurs, B., see Dammers-De Klerk, A.
Bové, J. 354
Breyer, B. and S. Hacobian 497
Bryan, H. A., see Dean, J. A.
Burt, R. and G. J. Minkoff 259
Buscaróns F. and J. Artigas 452
Callahan, C. M., W. C. Fernelius and B. P. Block 101
Cerletti, P., P. L. Ipata and N. Siliprandi 548
Chatterjee, K. K., see Basu, S.
Cimerman, Ch. and S. Frenkel 305
Codell, M., R. P. Egan and G. Norwitz 228
Codell, M. and G. Norwitz 327
Colichman, E. L., R. F. Fish and G. O. Bjarke 250
Coriou, H., J. Huré et J. Coursier . . 357
Coupez, J. 582
Coursier, J. see Coriou, H.
Crane, Jr., F. E. 370
Crimmin, W. R. C. 501
Daess, A. M., see Tourky, A. R.
Dahmen, E. A. M. F., see Van der Heijde, H. B.
Dammers-De Klerk, A. and B. Boot-Meurs 296
Datta, S. K. 115
Dean, J. A. and H. A. Bryan . 87, 94, 180
De Ligny, C. L., A. S. Hellendoorn, P. J. Seelen and D. Van Wijngaarden 516
Devanathan, M. A. V., Q. Fernando and P. Peries 292
Diehl, H., see Jaselskis, B.
Duval, C. 221, 545
Duyckaerts, G., see Sauvenier, Gh.
Edwards, J. W., see Milner, G. W. C.
Eeckhaut, J., see Leliaert, G.
Egan, R. P., see Codell, M.
Eisenstadter, J., see Bobtelsky, M.
Eldridge, J. S., see Schweitzer, G. K.
England, L. J., see Steele, M. C.
Fernando, Q., see Devanathan, M. A. V.
Fernelius, W. C., see Callahan, C. M.
Ficken, G. E. and E. S. Lane 207
Fish, R. F., see Colichman, E. L.
Frenkel, S., see Cimerman, Ch.
Gabrielson, G. and B. Andersson . . . 425
Geiger, R. A. and E. B. Sandell 346
Graham, R. P., see Page, J. A.
Grat-Cabanac, M. 150
Grosse, A. V., see Kirshenbaum, A. D.
Guedes de Carvalho, R. A. 555
Hacobian, S., see Breyer, B.
Hamdy, M., see Issa, I. M.
Hardy, C. J., see Pollard, F. H.
Heisig, G. B. and F. H. Pollard 234
Hellendoorn, A. S., see De Ligny, C. L.
Hewaidy, I. F., see Tourky, A. R.
Hibbs, L. E., see Wilkins, D. H.
Hoppe, T., see Bock, R.
Hourigan, H. F. and J. W. Robinson . 161
Hume, D. N. and I. M. Kolthoff 415
Hume, D. N., see Leonard, G. W.
Huré, J., see Coriou, H.
Ipata, P. L., see Cerletti, P.
Issa, I. M., H. Khalifa and M. Hamdy . 301
Issa, I. M., see Tourky, A. R.
Janssen, C. and G. B. Smit 276
Jaselskis, B. and H. Diehl 274
Jucker, H. 210
Keily, H. J., see Leonard, G. W.
Kertes, S. and M. Lederer 40
Keulemans, A. I. M., A. Kwantes and G. W. A. Rijnders 29
Khalifa, H., see Issa, I. M.
Kirshenbaum, A. D. and A. V. Grosse . 225
Kolthoff, I. M., see Hume, D. N.
Kotionis, A. Z., see Thomis, G. N.
Kovařík, M. and M. Moučka 249
Krogh-Svendsen, E., see Zimmermann, J.
Kwantes, A., see Keulemans, A. I. M.
Lane, E. S., see Ficken, G. E.
Langford, C. H., see Lingane, J. J.
Lederer, M., see Kertes, S.
Leliaert, G. and J. Eeckhaut 311
Leonard, G. W., H. J. Keily and D. N. Hume 185
Lingane, J. J. and A. J. Bard 271
Lingane, J. J., C. H. Langford and F. C. Anson 165
Lingane, J. J., see Page, J. A.
Lucena-Conde, F. and L. Prat 473
MacDonald, A. M. G., see Belcher, R.
Malmstadt, H. V. and D. A. Vassallo . 455
Mann, C. K. and J. H. Yoe 155
Manning, D. L., see Menis, O.
Maurice, M. J. 574, 578

Menis, O. and D. L. Manning 67
Milner, G. W. C. and J. W. Edwards 109
Minkoff, G. J., see Burt, R.
Mitra, S. P. and D. Prakash 431
Morgan, K. J., see Barltrop, J. A.
Moučka, M., see Kovařík, M.
Murthy, T. K. S. 25
Murty, G. V. L. N., T. S. Viswanathan and V. Ramakrishna 213
Nadkarni, M. N., M. S. Varde and V. T. Athavale 421
Nightingale, Jr., E. R. 493
Norwitz, G., see Codell, M.
Page, J. A. and J. J. Lingane 175
Page, J. A., D. H. Simpson and R. P. Graham 194
Pantony, D. A., see Blair, A. J.
Parry, E., see Belcher, R.
Peries, P., see Devanathan, M. A. V.
Picciotto, E. et S. Wilgain 530
Pollard, F. H. and C. J. Hardy 135
Pollard, F. H., see Heisig, G. B.
Prakash, D., see Mitra, S. P.
Prat, L., see Lucena-Conde, F.
Puchelt, H., see Umland, F.
Rafailoff, R., see Bobtelsky, M.
Ramaiah, N. A. and Vishnu 569
Ramakrishna, V., see Murty, G. V. L. N.
Ramana Rao, D. V. 1
Reimers, F., see Zimmermann, J.
Rieman, W., see Sargent, R. 144
Rijnders, G. W. A., see Keulemans, A. I. M.
Ringbom A., S. Siitonen and B. Saxén 541
Robinson, J. W., see Hourigan, H. F.
Rudloff, E. von 294
Ruggieri, R. 242, 246
Salaria, G. B. S. 3, 509
Sandell, E. B., see Geiger, R. A.
Sargent, R. and W. Rieman 144
Sauvenier, Gh. et G. Duyckaerts 592
Saxén, B., see Ringbom, A.
Scarano, E. 365
Schilt, A. A. and G. Frederick Smith 401
Schweitzer, G. K. and J. S. Eldridge 189
Seelen, P. J., see De Ligny, C. L.
Siitonen, S., see Ringbom, A.
Siliprandi, N., see Cerletti, P.
Simpson, D. H., see Page, J. A.
Sjöström, E. 428
Smit, G. B., see Janssen, C.
Smith, G. Frederick 505
Smith, G. Frederick, see Banick, Wm. M.
Smith, G. Frederick, see Schilt, A. A.
Stathis, E. C. 21
Steele, M. C. and L. J. England 148
Stevens, H. M. 435
Thomis, G. N. et A. Z. Kotionis 201
Tourky, A. R., I. M. Issa and A. M. Daess 81
Tourky, A. R., I. M. Issa and I. F. Hewaidy 151
Umland, F. und H. Puchelt 334
Van der Heijde, H. B. 392
Van der Heijde, H. B. and E. A. M. F. Dahmen 378
Van Wijngaarden, D., see De Ligny, C. L.
Varde, M. S., see Nadkarni, M. N.
Vassallo, D. A., see Malmstadt, H. V.
Vaughan, G. A., see White, D.
Vishnu, see Ramaiah, N. A.
Viswanathan, T. S., see Murty, G. V. L. N.
Wendlandt, W. W. 129, 216
Wetlesen, C. U. 268
White, D. and G. A. Vaughan 439
Wilgain, S., see Picciotto, E.
Wilkins, D. H. and L. E. Hibbs 449
Wilson, W. J. 419
Yoe, J. H., see Mann, C. K.
Yulius, I., see Bobtelsky, M.
Zimmermann, J., E. Krogh-Svendsen and F. Reimers 6

ANALYTICA CHIMICA ACTA Vol. 16 (1957)
SUBJECT INDEX

Chr. = Chromatography — chromatographie — chromatographische Analyse
Col. = Colorimetric, heterometric, photometric and spectrophotometric analysis (*) — colorimétrie, hétérométrie, photométrie et spectrophotométrie (*) — kolorimetrische, heterometrische, photometrische und spektrophotometrische Analyse (*)
El. = Electrical methods (except polarography) — Méthodes électriques (excepté polarographie) — Elektrische Methoden (ausgenommen Polarographie)
Grav. = Gravimetric and thermogravimetric (**) analysis — Gravimétrie et thermogravimétrie (**) — gravimetrische und thermogravimetrische (**) Analyse
Id. = Identification reactions and qualitative analysis — identification (réactions) et analyse qualitative — Identifizierungsreaktionen und qualitative Analyse
M. = Miscellaneous — divers — Verschiedenes
Pol. = Polarography — polarographie — Polarographie
Vol. = Volumetric analysis — volumétrie — volumetrische Analyse

	Chr.	Col.	El.	Grav.	Id.	M.	Pol.	Vol.
Acetic anhydride								520
Acid-base-titration			365					
Acide quinoléine-8-carboxylique						332		
Acide(s)			378 392					
Acide tribasique			274					
Adenin(e)	548		548					
Adenosin(e)	548		548					
Ag	234							
Al.	234 421	148					87 94 194	
Alcali-acidimétrie			365					
Alcaloïdes, Alkaloide					201			
Anhydride acétique								520
Antipyrin(e)	428							
Argile	431							
As.	234	473		3				
Au						479		
Azogroup, -gruppe								210
Ba.	234				6			
Basen, bases			378					
Bases azotées					201			
Be.	421							
Bi.	234	488						
Bois.								419
Bromat(e)			81					
Ca.	234	569*			6	311		
Cacothelin(e).								415
Caféine, caffein	428							
Ce.			81 185					
Cd.	234						87	
Chelat(e)			501					
Chinoidgruppe								210
Chinolin-8-carbonsäure						332		
Chlorid(e), chlorure	425							524
Chromat(e)		452						
Clays	431							
Co	234 449	449				101	87 94	
Combustion products, produits, Produkte		259*						
Coulometer, coulomètre			175					

	Chr.	Col.	El.	Grav.	Id.	M.	Pol.	Vol.
Courbes de polarisation			285					
Cr.	234					40		
Cu.	121 234 435	121* 464 268 401		21		332		516
Diethylthiocarbamat(e)		488				479		
2,2′-Dipyridin(e)		401						
Dreibasische Säure			274					
Eau			582					520
Électrodes, Elektroden			365 493					
Électrolyse, electrolysis, Elektrolyse			357					
Entonnoir à séparation						505		
Essigsäureanhydrid								520
Étalons				221** 545**				
Exchange resins								207
F						213		213
Fe.	234 421	150 464 242 401				541	87 94	415
Ferricyanid(e), ferricyanure			81					
Float siphon						351		
Ge.		473					592	
Glycol	144							
Groupements azo, nitro, nitroso, quinoïdes								210
Halogenated hydrocarbons	135							
Halogenierte Kohlenwasserstoffe	135							
Hg	231 234			3				301 305
Holz								419
Hydrocarbon	29							
Hydrocarbures	29							
Hydrocarbures halogénés	135							
Hydroxy-8-quinoléine						334		
8-Hydroxyquinolin(e)						334		
Hypoxanthin(e)	548		548					
Indicateur, Indicator, Indikator								415
Inosin(e)	548		548					
Iodide, iodure			165					
Ionenaustauscherharzen								207
Jodid.			165					
K	234							
Kaffein.	428							
Katharometer, katharomètre	29							
Kohlenwasserstoffe	238		238					
Localisation des zones	238		238					
Methoxyl.						294		
Mg	234	155*	180				87 94	

	Chr.	Col.	El.	Grav.	Id.	M.	Pol.	Vol.
Micas, Mika	431							
Mn	234	151					87 94	
Mo		75			3			
Na	234	161 488	292					
Neutralisationstitrationen			365					
NH_4^+	234							
Ni							87 94	
Nitrat(e)	425							
Nitrogroup, -gruppe								210
Nitrosogroup, -gruppe								210
Nitrosonapht(h)ol(s)						101		
O			276			225 296		
Organic bases					201			
Organic substances								210
Organische Basen					201			
Organische Verbindungen								210
Oxin(e)						334		
8-Oxychinolin						334		
P		473						
Paramolybdat(e)						1		
Pb	234	321						
Pd						479		
Phenole, phenols	439							
Polarisationskurven			285					
Polarization curves			285					
Polyiodides, Polyjodiden					406			
Polyiodures					406			
Polyphenyl(s)						250		
Pontachrome violet SW							87 94	
Pontachrome violett SW							87 94	
Pt	449	449						
Quinoid group								210
Quinoline-8-carboxylic acid						332		
Radioactivité, radioactivity, Radioaktivität						189		
Radionuclides						189		
Résines								207
R_F	555							
S		574*						
Säuren			378 392					
Sb	234		271					
Sc		334						
Separatory funnel						505		
Si		67* 327		327				
Siphons à flotteur						354		
Sn	234							
Sr	234					311		
Standards				221** 545**				

	Chr.	Col.	El.	Grav.	Id.	M.	Pol.	Vol.
Substances organiques								210
Sulfat(e), sulphate					6			
Te				3				
Terphenyl, terphenyl(e)s					250			
Tetraphenylborat(e)			370					
Th		56*				530		115
Thiosalts, Thiosalze					509			
Thiosels					509			
Thiosulfat(e), thiosulfate			292					
Ti	421					228		
Titrator, titreur		455*						
Tl				216	249			
Tonerde	431							
Trennungstrichter			274					
Tribasic acid			274					
Tungstat(e)			497					
U	25	44						109
V	25	246						
Vergleichssubstanzen				221** 545**				
Vin		464*						
Violet pontachrome SW							87 94	
Wasser, water			582					520
Wein, wine		464*						
Wood								419
Zn	234						87	516
Zone localization	238		238					419
Zonen Lokalisierung	238		238					
Zr		62* 346		129**				

PARAMOLYBDATES OF ORGANIC BASES

by

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INTRODUCTION

Molybdate ion exists in solution in different states of aggregation, depending upon the pH range. When acid is added to a molybdate solution, progressive aggregation of negative ions takes place as their negative charge gets neutralized by hydrogen ions. The tri-molybdate ion exists over the pH range 6.3-4.5. After that up to pH 1.5, paramolybdates are stable[1]. In a critical review on the polymolybdates, CARPÉNI reports[2] two possible mole ratios (5:12) and (3:7) for $R_2O:MoO_3$ for the paramolybdates without any final decision. LINDQVIST'S analytical results on ammonium paramolybdate suggest[3] the formula $3\ (NH_4)_2O\cdot 7\ MoO_3\cdot 4\ H_2O$. The important X-ray investigation on the ammonium paramolybdate by STURDIVANT also indicated[4] the formula $(NH_4)_6(Mo_7O_{24})\cdot 4\ H_2O$. JANDER[1] from his studies in solutions, however, showed the presence of MoO_{21}^{-6} ion. In an earlier communication[5] the composition of the compound separated at pH 2 could not be definitely fixed up. The differences in the ratio of $R_2O:MoO_3$ for the alternative formulae can be enhanced and made clear if R is a cation of high ionic weight. With this idea in view, the present work was carried out with several organic bases.

EXPERIMENTAL

A concentrated aqueous solution of sodium molybdate was prepared and a solution of pyridine in hydrochloric acid was added. No precipitate was obtained and the pH of the mixture was 8.2. Hydrochloric acid was added to this mixture of solutions. A white precipitate was formed when the pH of the solution was nearly 1.5. This precipitate was transferred to a filter paper and washed with a buffer solution (pH 1.5) and finally with ether. No reduction of the molybdenum compound to the blue stage occurred during drying and hence the moist precipitate was dried in an air oven at 105°C to a constant weight. A weighed sample of the dried complex was heated in a porcelain crucible. Pyridine distills off and the mass turns bluish. A few drops of concentrated nitric acid were added and again ignited. Heating was done cautiously since the oxide MoO_3 sublimes at bright red heat[6]. The white residue of molybdic oxide was cooled in a desiccator and weighed.

Quinoline and dimethylaniline compounds of molybdenum were also prepared in the same way and similar estimations were carried out to establish their composition. The aim of the present work is to ascertain the composition of the precipitated compound.

RESULTS AND DISCUSSION

Several estimations were carried out but only the results obtained in one set of experiments are given below. All the estimations gave concordant results. The amount of nitrogen was also estimated in the case of the pyridine compound by Kjeldahl's method and the results obtained indicate the same conclusion. Hence it was not determined in the other two cases.

Pyridine compound

0.2936 g of the compound when converted into the oxide gave 0.2262 g of MoO_3. This is equivalent to 0.1508 g of molybdenum. Hence one gram atom of molybdenum (95.95 g) will be present in 186.8 g of the compound. $(PyH)_3H_3Mo_7O_{24}$ and $(PyH)_3H_3Mo_6O_{21}$ require 185 and 192 g of the compound per gram atom of molybdenum respectively. One gram atom of nitrogen on similar calculation was found to be present in 424 g of the compound. The above two formulae require 433 and 385 g respectively.

Quinoline and dimethylaniline compounds

	Quinoline compound	*Dimethylaniline compound*
Compound taken (g)	0.2863	0.2774
Molybdic oxide obtained (g)	0.2058	0.1974
Molybdenum equivalent (g)	0.1372	0.1316
Compound containing one gram atom of molybdenum	200.2	202.2
Theoretical amount according to		
(a) $(Quin.H/Dimeth.H)_3H_3Mo_7O_{24}$	206	203
(b) $(Quin.H/Dimeth.H)_3H_3Mo_6O_{21}$	217	213

Thus the analyses of these three compounds reveal that the paramolybdates are precipitated and the results are more in favour of the presence of $Mo_7O_{24}^{-6}$ than $Mo_6O_{21}^{-6}$ ion in the solid state. This is also in agreement with an earlier communication[7] on the composition of dipyridyl paramolybdate. All these results relate to the analyses of solid compounds. But JANDER when working with solutions could not detect the $Mo_7O_{24}^{-6}$ ion and this failure of JANDER to find evidence for Mo_7 anion in solution suggests[8] that some kind of hydrolysis takes place which can be represented as follows:

$$[Mo(Mo_6O_{24})]^{-6} + H_2O \rightleftharpoons [Mo_6O_{21}]^{-6} + H_2MoO_4.$$

This requires further investigation and confirmation.

ACKNOWLEDGEMENT

Thanks are due to Dr. S. PANI for his helpful criticism and to the Board of Scientific and Industrial Research, Orissa, for a grant.

SUMMARY

Pyridine, quinoline and dimethylaniline form insoluble paramolybdates near pH 1.5. On analysis, these compounds reveal the presence of a $Mo_7O_{24}^{-6}$ ion but not a $Mo_6O_{21}^{-6}$ ion and this is in conformity with the earlier X-ray investigations of paramolybdates.

RÉSUMÉ

La pyridine, la quinoléine et la diméthylaniline forment des paramolybdates insolubles à un pH d'environ 1.5. L'analyse de ces composés confirme la présence de l'ion $Mo_7O_{24}^{-6}$, mais non celle de $Mo_6O_{21}^{-6}$; ceci correspond aux résultats obtenus lors des recherches sur les paramolybdates par les rayons X.

ZUSAMMENFASSUNG

Pyridin, Chinolin und Dimethylanilin bilden bei einem pH von ungefähr 1.5 unlösliche Paramolybdate. Die Analyse dieser Verbindungen ergab die Gegenwart von $Mo_7O_{24}^{-6}$ und nicht $Mo_6O_{21}^{-6}$, was mit den Ergebnissen früherer Röntgenstrahlen-Untersuchungen von Paramolybdaten in Übereinstimmung ist.

References p. 3.

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SEPARATIONS INVOLVING SULPHIDES

II. SEPARATION OF ARSENIC, MOLYBDENUM AND TELLURIUM FROM MERCURY

by

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In a previous publication[1] of this series, separations of some metals of the arsenic group from barium were investigated and it was shown that the separations are fairly satisfactory. In the present investigations separations of some metals of the arsenic group from mercury have been studied. The solution containing the two metals is treated with an excess of the alkali sulphide reagent and the thiosalt formed by mercury is then decomposed by treatment with ammonium acetate at a low temperature[2]. In another portion of the solution, containing the two metals after treatment with alkali sulphide reagent, the thiosalts of both the metals are decomposed with hydrochloric acid and the precipitated sulphides of the two metals are weighed together. The weight of the sulphide of the arsenic group metal is determined by difference. It is not possible to estimate the metal of the arsenic group in the filtrate from mercuric sulphide, owing to atmospheric oxidation of the reagent during washing, which gives high results. The estimation of the two metals does not take more than three hours.

EXPERIMENTAL

Separation of arsenic from mercury

Measured portions of standard solutions of mercuric chloride[3,4] (AnalaR quality) and potassium arsenate[5] were mixed together and the precipitate of mercuric arsenate was dissolved in the minimum quantity of hydrochloric acid. In one set of experiments the solution was treated with a large excess of $2N$ sodium sulphide reagent[6] and the thiosalt of mercury was decomposed by adding an excess of ammonium acetate (solid) in the cold. The mixture was shaken for a minute to complete the precipitation of mercuric sulphide, filtered through a weighed sintered glass crucible (porosity 4) and washed thoroughly with distilled water, alcohol and ether successively. It was dried in an air-oven at 105°C for an hour and weighed as HgS. In another set of experiments the mixture of the thiosalts formed with alkali sulphide reagent was treated with an excess of concentrated hydrochloric acid, the concentration of the acid in the resulting mixture was adjusted at a little above $6N$, the mixture heated to boiling, and allowed to cool to room temperature. The mixed precipitate of the sulphides was filtered through a weighed sintered glass crucible (porosity 4) washed thoroughly with distilled water, alcohol and ether successively, dried in an air-oven at 105°C for an hour and weighed. The weight of the precipitated arsenic pentasulphide was determined by subtracting the weight of mercuric sulphide from the weight of the mixed sulphides.

The results are given in Table I.

TABLE I

DETERMINATION OF ARSENIC AND MERCURY IN A MIXTURE WITH 2*N* SODIUM SULPHIDE REAGENT

Vol. of Hg solution ml	*Vol. of As solution ml*	*Vol. of 2N Na_2S added ml*	*Vol. of 12N HCl added ml*	*Wt. of Hg in HgS g*	*Wt. of Hg actually present g*	*Wt. of As in As_2S_5 g*	*Wt. of As actually present g*
25	25	60	120	0.1858	0.1859	0.09020	0.09024
25	10	45	90	0.1854	0.1859	0.03596	0.03610
10	25	45	95	0.07432	0.07437	0.09016	0.09024
10	10	35	60	0.07440	0.07437	0.03599	0.03610
5	10	20	40	0.03725	0.03718	0.03604	0.03610
10	5	30	50	0.07423	0.07437	0.01803	0.01805

Separation of molybdenum from mercury

Measured portions of standard solutions of mercuric chloride[3,4] (AnalaR quality) and ammonium molybdate[7] were mixed together. The precipitate of the mercuric molybdate formed was dissolved in the minimum quantity of hydrochloric acid. It was then treated with a large excess of 2*N* sodium sulphide reagent[6]. In one set of experiments the mixture of the thiosalts formed with alkali sulphide reagent was treated in the cold with an excess of ammonium acetate (solid), shaken for a minute to complete the precipitation of mercuric sulphide, filtered through a weighed sintered glass crucible (porosity 4) and after suitable treatment weighed as HgS. In another set of experiments the mixture of the thiosalts formed with alkali sulphide reagent was treated with a large excess of 2*N* hydrochloric acid, the concentration of the acid in the resulting mixture adjusted at approximately 1*N*, the mixture heated to boiling and allowed to cool to room temperature. The mixed precipitate of the sulphides was filtered through a weighed sintered glass crucible (porosity 4), washed thoroughly with distilled water, alcohol and ether successively, sucked dry at the filter pump for 15 minutes, dried in a vacuum desiccator for an hour and weighed.

The weight of the precipitated molybdenum sulphide, was determined by subtracting the weight of mercuric sulphide from the weight of the mixed sulphides. The results are given in Table II.

TABLE II

DETERMINATION OF MOLYBDENUM AND MERCURY IN A MIXTURE WITH 2*N* SODIUM SULPHIDE REAGENT

Vol. of Hg solution ml	*Vol. of Mo solution ml*	*Vol. of 2N Na_2S added ml*	*Vol. of 2N HCl added ml*	*Wt. of Hg in HgS g*	*Wt. of Hg actually present g*	*Wt. of Mo in sulphide ppt. g*	*Wt. of Mo actually present g*
25	25	60	130	0.1859	0.1859	0.06990	0.06998
25	25	75	145	0.1857	0.1859	0.07011	0.06998
10	25	70	115	0.07432	0.07435	0.06982	0.06998
5	25	55	110	0.03716	0.03717	0.06995	0.06998
25	20	70	140	0.1857	0.1859	0.05602	0.05599
25	10	50	105	0.1856	0.1859	0.02797	0.02800

Separation of tellurium from mercury

Measured portions of standard solutions of mercuric chloride[3,4] and potassium tellurite[8] were mixed together, the precipitate of mercuric tellurite formed was dissolved in the minimum quantity of hydrochloric acid and treated with a large excess of 2*N* sodium sulphide reagent[6].

In one set of experiments the mixture of the thiosalts formed with alkali sulphide reagent was treated in the cold with an excess of ammonium acetate (solid), shaken for a minute to complete the precipitation of mercuric sulphide, filtered through a weighed sintered glass crucible (porosity 4) and after suitable treatment weighed as HgS. In another set of experiments the mixture of the thiosalts formed with alkali sulphide reagent was treated with a large excess of 2*N* hydrochloric acid sufficient to produce a concentration of approximately 1N, the mixture heated to boiling and allowed to cool to the room temperature. The mixed precipitate of the sulphides was filtered through a weighed sintered glass crucible (porosity 4), washed thoroughly with distilled water, dried at 105°C for an hour and weighed.

The weight of the precipitated tellurium sulphide, TeS_2, was determined by subtracting the weight of mercuric sulphide from the weight of the mixed sulphides.

The results are given in Table III.

TABLE III

DETERMINATION OF TELLURIUM (TETRA-VALENT) AND MERCURY IN A MIXTURE WITH 2N SODIUM SULPHIDE REAGENT

Vol. of Hg solution ml	*Vol. of Te solution ml*	*Vol. of 2N Na_2S added ml*	*Vol. of 2N HCl added ml*	*Wt. of Hg in HgS g*	*Wt. of Hg actually present g*	*Wt. of Te in TeS_2 g*	*Wt. of Te actually present g*
25	25	55	115	0.1861	0.1864	0.05253	0.05259
20	25	40	110	0.1489	0.1491	0.05272	0.05259
20	25	45	105	0.1490	0.1491	0.05253	0.05259
25	20	50	110	0.1862	0.1864	0.04194	0.04207
10	25	45	90	0.07457	0.07457	0.05253	0.05259
25	10	40	90	0.1862	0.1864	0.02104	0.02104

The method is also applicable to a mixture of mercury and tellurium when the latter is present in the hexavalent state. But in this case the mixture of the thiosalts has to be decomposed with concentrated hydrochloric acid and tellurium estimated as TeS_3[9].

SUMMARY

It has been shown that it is possible to determine arsenic, molybdenum or tellurium in the presence of mercury by decomposing in one portion the thiosalt of mercury alone with ammonium acetate and in another portion the thiosalts of both the metals with hydrochloric acid.

RÉSUMÉ

Il est possible de doser l'arsenic, le molybdène ou le tellure, en présence de mercure, en décomposant, sur une partie aliquote, le thiosel de mercure seul au moyen d'acétate d'ammonium, et sur une autre partie, les thiosels des deux métaux par l'acide chlorhydrique.

ZUSAMMENFASSUNG

Arsen, Molybdän und Tellur können in Gegenwart von Quecksilber bestimmt werden, indem man erst, in einem Teil der Lösung, das Quecksilberthiosalz allein mit Ammoniumacetat zersetzt und dann, in einem anderen Teil, die Thiosalze beider Metalle mit Salzsäure zerstört.

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LIMIT TESTS FOR IMPURITIES
IV. INVESTIGATIONS INTO THE REPRODUCIBILITY OF PRECIPITATION PART III*

by

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In previous papers it has been shown that the reproducibility of turbidities formed in precipitation of barely soluble substances is often so limited that the turbidimetric purity tests from many pharmacopoeias present a very uncertain basis for assessment of the content of impurities in medicinal products.

An improvement of the reproducibility can easily be obtained as far as precipitation of soft crystals (*e.g.* silver chloride and lead sulphide) is concerned. It is necessary only to make sure that the rate of mixing of the test solution and the reagent is constant. Improvement in the reproducibility of precipitation of hard crystals (*e.g.* barium sulphate and calcium oxalate) is obtained by precipitation during seeding[1].

The improved tests are used in *Ph. Dan.* 1948, in Addendum I (1953) to *Ph. Norv.* 1939, and, somewhat modified, in *Ph. Hung.* 1954.

In this work the results of attempts towards further improvement of reproducibility of precipitation of barium sulphate and calcium oxalate are described. A brief introductory description of certain of the chief points in the theory of precipitation of crystals is given in order to provide a means of orientation.

The processes which occur when precipitation of barium sulphate and calcium oxalate is used as a basis for purity tests can be divided into 3 phases: 1) Nucleation, 2) Growth of the nuclei, 3) Possible ageing of the crystals.

Nucleation. The presence of *e.g.* barium and sulphate ions in a liquid at intervals corresponding to those in barium sulphate crystals will not always result in crystal formation because the ions will have a tendency to redissociate. It is only when the number of ions has reached a certain critical size that a nucleus is formed whose tendency to grow is greater than the tendency to redissolve. CHRISTIANSEN AND NIELSEN[2] have shown that the time of formation of visible precipitation in as olution containing equivalent quantities of the ions reacting may be expressed as: $t \cdot c_0^{p-1} = k$, where c_0 is the ion concentration, p and k are constants. For barium sulphate they find that $t \cdot c_0^7 = 10^{-11.8}$; however, the exponent of c_0 may possibly be 6. They conclude from this that the nuclei of barium sulphate contain 8 ions, which is many fewer than formerly presumed (see *e.g.* FRENKEL[3]).

Growth. The growth of the nuclei formed depends upon many conditions, among others upon the concentration of the ions reacting. If other conditions are constant the rate of growth is proportional to the size of the surface of the crystals. Therefore the rate of growth increases rapidly in the beginning in such a way that the period of induction, during which nucleation occurs, is concluded rather abruptly, and visible precipitation occurs. Growth brings about a lessening of the concentrations of the reacting ions. As the rate of formation of nuclei is, as mentioned, proportional to the ion concentration to a high power, whilst the rate of growth is proportional to the concentration to a lower power[4], nucleation will rapidly cease, and the growth will continue with a speed which gradually decreases as the result of reduction of concentration of the reacting ions. It follows from this that in precipitation the nuclei will normally be formed at nearly the same time, and that the crystals will therefore be of nearly the same age and thus be of nearly the same size.

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* For Parts I and II, see *Acta Pharm. Intern.*, 1 (1950), 55, 139.

Ageing. The crystals formed can, on standing in the mother liquor, change in 3 ways: by agglutination, by OSTWALD's recrystallization[5], and by recrystallization as the result of wandering of the ions in the liquid film which surrounds the crystal[6]. The first-mentioned form of recrystallization occurs, according to FISCHER[7] only when the crystals are very small, less than 1 μ. All these changes may cause a change in the visibility of the precipitate.

If an attempt is to be made to carry out precipitation of a barely soluble crystalline substance in such a way that incidental factors (the initiating action of undissolved impurities or of the surface of the container) have the least possible influence, it seems probable that an effort must be made to achieve the quickest possible formation of nuclei and the formation of a relatively large amount of nuclei, so that the crystals become relatively small, and their total surface, and thus their rate of growth, great. However, care must be taken that the number of nuclei does not become too great, so that the precipitated crystals are so small that their visibility is too scanty.

As a means of attaining precipitation according to the desired fashion, raising the concentration of the reagent and lessening the solubility of the precipitated substance may be considered. Already VON WEIMARN[8] has shown that barium sulphate precipitates as finer crystals when its solubility in the medium is reduced by addition of alcohols. Precipitation in the presence of ethanol is therefore one method of procedure which may be expected to lead to formation of a larger number of nuclei (*cf.* ILVER, JACKEROTT AND REIMERS[9]). VOGELENZANG[10] has suggested the use of ethanol-containing seeding reagents in the precipitation of, among others, sulphate, barium and calcium. With these suggestions, published after our investigations were nearly concluded, we shall be concerned in a following publication.

It should be remembered that added substances may often affect precipitation in several different ways *e.g.* by altering the solubility, by altering the rate of growth as a result of adsorption onto the crystal surfaces, by changing the viscosity and by this means the rate of diffusion, and lastly by altering the refractive index of the fluid and thus the visibility of the precipitate.

In the investigation described below nephelometer values, determined by means of a Coleman photo-nephelometer, model 7, are used as a measure of turbidity. The mean value $\bar{x}$ and the relative standard deviation $s_{\text{rel}} = 100\ s/\bar{x}$ are calculated from the nephelometric values determined in n identical separate experiments. It should be remembered that the scattering of light, measured in the nephelometer, cannot directly be taken as an expression of the visibility of the precipitate which is determined by both the Tyndall effect and the absorption of light. Both these conditions depend upon particle size, but in different ways.

I. LIMIT TEST FOR SULPHATE

a. Detection of sulphate without seeding

Some of the results of a systematic investigation into the precipitation of sulphate by means of barium chloride reagents without seeding are reproduced in Table I.

TABLE I

THE PRECIPITATION OF BARIUM SULPHATE BY BARIUM CHLORIDE REAGENT WITHOUT SEEDING

10 ml test solution + 1 ml 1*M* hydrochloric acid + 1 ml reagent. The test solution is poured into the reagent (T in R) or vice versa (R in T). $n = 20$.

Test solution		*$BaCl_2$*	*Treatment*	*5 min*		*10 min*	*30 min*
Salt	*SO_4^{-2} µg/ml*	*M*		$\bar{x}$	s_{rel}	$\bar{x}$	$\bar{x}$
Absent	5	0.25	T in R, mixed	62.5	37.3	74.1	79.2
	2.5	0.5	T in R, mixed	54.2	21.0	67.2	75.2
	2.5	1	T in R, mixed	49.6	17.7	54.5	54.5
	5	0.25	T in R, shaken	79.9	17.0	90.5	94.4
	2.5	1	T in R, shaken	30.0	14.3	32.1	32.9
	5	1	R in T, shaken	54.5	8.4	59.1[a]	62.9[a]
5% NaCl	10	0.25	T in R, mixed	22.2	54.5	47.5	80.9
	5	0.5	T in R, mixed	16.2	65.9	24.8	38.0
	5	1	T in R, mixed	22.5	43.8	35.8	47.5
	10	0.25	T in R, shaken	46.8	28.2	78.6	100.6
	5	1	T in R, shaken	26.6	22.6	30.6	33.8
	10	0.25	R in T, shaken	14.7	23.2	39.9	70.2
	5[b]	1	R in T, shaken	27.5	5.0	29.2	
	5[c]	1	R in T, shaken	25.6	5.1	31.7	35.7
5% KNO_3	16	1	R in T, shaken	68.7	11.0	ca. 130[a]	>130[a]
	6[d]	1	R in T, shaken	51.4	16.6	79.9[a]	93.2[a]

[a] $n = 5$.
[b] Analyst A.
[c] Analyst B.
[d] 1 ml 2*M* acetic acid added instead of hydrochloric acid.

It is seen that the reproducibility is extremely poor when precipitation is carried out so that shaking of the mixture of the test solution and reagent is avoided: the whole of the test solution is poured at the same time over the reagent, after which the mixture is stirred carefully. Shaking improves the reproducibility to a certain extent, but really satisfactory results can only be obtained by precipitation with 1*M* $BaCl_2$, which is poured into the test solution, after which it is shaken vigorously. This procedure gives, moreover, a rapid rate of precipitation. It must be presumed that the reason why precipitation with 1*M* $BaCl_2$ gives reproducible results is that the barium ion concentration is so high in the zone where reagent and test solution are mixed immediately after addition of the reagent that nuclei are formed very rapidly. However, by precipitation in potassium nitrate solution sensitivity, rate of precipitation, and reproducibility are somewhat reduced. Acidification with 1*M* acetic acid (*cf. Ph. Jugosl.* 1951) improves the sensitivity, but not the reproducibility.

In precipitation without shaking increasing the quantities of test solution to 50 ml (*cf.* among others *B.P.* 1953) or to 250 ml does not alter the results.

In the experiments where s_{rel} is very large on reading after 5 minutes' standing it will be less on reading after standing for a longer time. Thus it was found by the experiments with 5% NaCl solution and 0.5*M* $BaCl_2$ that after 5 min $s_{rel} = 65.9$, after 10 min $s_{rel} = 38.4$, and after 30 min $s_{rel} = 20.4$. In experiments where s_{rel} is small the values found after standing for 5, 10 and 30 min differ only slightly.

In precipitation with 1*M* $BaCl_2$ which is added to the test solution the results will be the same whether the mixture is shaken immediately after mixing, or the shaking is postponed for 15-30 sec. The addition of 5% v/v ether or 10% v/v ethanol to the test solution alters the results only slightly.

The significance of the temperature is seen in the following experiment: with a 5% NaCl solution, containing 10 µg/ml SO_4^{-2}, the findings were at approximately 13° $x = 59.6$ (5 min) and 65.9 (10 min), and at approximately 23° $x = 88.9$ (5 min) and 95.1 (10 min) ($n = 10$).

1*M* $BaCl_2$ prepared from several different samples of barium chloride manufactured by E. Merck for analytical purposes, contained impurities which seed out the precipitation of $BaSO_4$ in 5% KNO_3 solution. In an investigation of the above-mentioned solution with 10 µg/ml SO_4^{-2} a non-filtered 7 hour old $BaCl_2$ solution gave $x = 90.9$, a freshly prepared filtered solution gave $x = 75.3$, the same solution 7 hours later gave $x = 28.8$. A reagent filtered after standing for 7 hours gave $x = 9.9$ (5 min, $n = 3$). With a 48 hours old filtered reagent $x = 3.2$. The reagent should therefore be left to stand for at least 24 hours and then be filtered. On precipitation in 5% NaCl solution these impurities do not alter the result. This is probably due to the fact that in this case nucleation and growth of the crystals occur so quickly that the seeding impurities cannot influence the course of precipitation to any great extent. Also Steinbergs[11], Fischer and Rhinehammer[12], Bogan[13], Benedetti-Pichler[14], and O'Rourke and Johnson[15] have been able to establish in different ways the fact that $BaCl_2$ solutions contain seeding impurities.

b. Detection of sulphate with seeding reagents not containing ethanol

In the experiments in Table II the precipitation method suggested earlier[1] is compared with precipitation with a seeding reagent prepared from 1*M* $BaCl_2$. Precipitation is carried out in the following manner: 1 ml $BaCl_2$ reagent is added to 1 drop of a K_2SO_4 standard solution containing the stated amount of SO_4^{-2}. After standing for 1 min precipitation of a small quantity of $BaSO_4$ in this seeding reagent is concluded. Then a mixture of 10 ml test solution and 1 ml 2*M* hydrochloric acid is added, and the mixture is shaken vigorously for 10 sec.

TABLE II

THE PRECIPITATION OF BARIUM SULPHATE BY BARIUM CHLORIDE SEEDING REAGENT NOT CONTAINING ETHANOL

10 ml test solution + 1 ml 2*M* hydrochloric acid + seeding reagent prepared from 1 drop sulphate standard solution and 1 ml $BaCl_2$ solution. $n = 20$.

Test solution		*Seeding reagent*		*5 min*		*10 min*	*30 min*
Salt	SO_4^{-2} µg/ml	SO_4^{-2} µg/ml	$BaCl_2$ *M*	x	s_{rel}	x	x
Absent	5	100	0.25[a]	80.5	14.1	86.0	87.6
	5	25	1[b]	68.8	5.9	68.7	68.7
5% NaCl	10	100	0.25	76.4	20.0	90.8	105.7
	10	25	1	71.0	10.4	72.3	73.9
5% KNO_3	20	100	0.25	35.5	37.0		
	8	25	1	49.3	42.4	117.2[c]	>130[c]

Blank values (seeding reagent + 11 ml water):
[a] $x = 9.6$ (5 min, $n = 5$)
[b] $x = 10.1$ (5 min, $n = 9$)
[c] $n = 5$.

It is seen that the increase in the barium ion concentration is accompanied by an increase of rate of precipitation and of reproducibility. The results, however, are no better than in precipitation with 1 M $BaCl_2$ without seeding.

If 5% v/v ether or 10% v/v ethanol are added to the test solution, the results are only slightly altered. In the presence of a larger content of ethanol (20-40% v/v) the precipitated particles are smaller, and the nephelometer values higher, but the reproducibility is not improved.

c. Detection of sulphate by means of seeding reagents prepared from ethanol-containing barium chloride reagents

Whilst, as mentioned, the presence of ethanol in the test solution does not cause appreciable improvement in reproducibility, the use of ethanol-containing barium chloride solution causes a clear reduction of the s_{rel} values. At an ethanol content of 10-20% v/v, $BaSO_4$ is precipitated as relatively coarse crystals, in the same way as in precipitation in pure aqueous solution, whereas the precipitate is finer with ethanol concentrations of 30% v/v and more. Experiments with higher concentrations than 50% v/v have not been carried out, as 0.25 M $BaCl_2$ with larger ethanol concentration will cause precipitation on standing. Table III shows that especially seeding reagents prepared from 0.25 M $BaCl_2$ with 50% v/v ethanol give good results.

TABLE III

THE PRECIPITATION OF BARIUM SULPHATE WITH SEEDING REAGENT PREPARED FROM ETHANOL-CONTAINING BARIUM CHLORIDE SOLUTION

10 ml test solution + 1 ml 2M hydrochloric acid + seeding reagent prepared from 1 drop of sulphate standard solution (100 µg/ml SO_4^{-2}) and 1 ml ethanol-containing 0.25M $BaCl_2$. $n = 20$.

Test solution		*Ethanol in the reagent*	*5 min*		*10 min*	*30 min*
Salt	*SO_4^{-2} µg/ml*	*% v/v*	$\bar{x}$	s_{rel}	$\bar{x}$	$\bar{x}$
Absent	5	30	82.4	10.5	86.7	82.8
	5	50[a]	75.4	3.7	75.8	74.8
5% NaCl	10	30	89.7	15.0	104.7	110.3
	10	50	79.2	5.4	83.4[b]	
5% KNO_3	10	50	41.2	9.4	57.5[b]	88.2[b]

[a] Blank value (seeding reagent + 11 ml water): $\bar{x} = 9.1$ (5 min, $n = 5$).
[b] $n = 5$.

The results with this reagent are affected only slightly by altering the temperature. The findings with a 10 µg/ml SO_4^{-2} in 5% NaCl solution at approx. 12° are: $\bar{x} = 71.3$, at approx. 28° : $\bar{x} = 75.8$ (5 min, $n = 5$).

If the seeding reagent is prepared from 1 ml of a more dilute sulphate standard solution (10 µg/ml SO_4^{-2}) the reproducibility is lessened ($s_{rel} = 11.1$ (5 min)). This is due to the fact that the $BaSO_4$ in separate experiments which give higher nephelometer values is precipitated as finer particles (the suspension turns a bluish colour).

d. Detection of sulphate with seeding reagents prepared from ethanol-containing sulphate standard solutions

If ethanol is present in the sulphate standard solution it has a still greater influence on precipitation. If the solutions used contain 10-20% v/v ethanol the $BaSO_4$ is precipitated as relatively coarse crystals, with 30% v/v it shows a bluish opales-

References p. 21.

cence, and with 40-50% v/v the particles become so fine that the opalescence formed is only faintly visible.

Experiments with sulphate standard solution with 30% v/v ethanol, in which the $BaCl_2$ concentration is varied, have shown that $1M$ $BaCl_2$ gives better reproducibility than $0.1M$ $BaCl_2$. As seen in Table IV an especially satisfactory reproducibility is obtained with $1M$ $BaCl_2$ and ethanol-containing sulphate standard solution, even by precipitation in KNO_3 solution.

TABLE IV

THE PRECIPITATION OF BARIUM SULPHATE WITH SEEDING REAGENT PREPARED FROM ETHANOL-CONTAINING SULPHATE STANDARD SOLUTION

10 ml test solution + 1 ml $2M$ hydrochloric acid + seeding reagent prepared from 5 drops of sulphate standard solution (100 μg/ml SO_4^{-2} in 30% v/v ethanol) and 1 ml $1M$ $BaCl_2$.

Test solution		*5 min* *(n = 20)*		$\bar{x}$ (*n* = 5)		
Salt	SO_4^{-2} *µg/ml*	*x*	s_{rel}	*5 min*	*10 min*	*30 min*
Absent	2	48.0	10.1	47.1	47.7	44.2
5% NaCl	2[a, b]	47.8	3.4	48.8	53.0	55.0
5% NaCl	2[c]	28.6	5.2			
5% KNO_3	5	70.3	3.5	69.5	91.0	114.6

[a] Blank value (seeding reagent + 11 ml water): $\bar{x}$ = 15.2 (5 min, n = 5).
[b] Analyst A.
[c] Analyst B.

The difference between the results obtained by analyst A and analyst B may be due to a difference in temperature; with 2 μg/ml SO_4^{-2} in 5% NaCl solution the findings were at approx. 12° : $\bar{x} = 24.9$, at approx. 32° : $\bar{x} = 44.4$ ($n = 5$).

e. Comparison of the limit tests for sulphate

In the experiments described above the following tests have proved to be most promising:

I. Precipitation by $1M$ $BaCl_2$ which is added to the test solution.
II. Precipitation by seeding reagent prepared from 1 drop of sulphate standard solution (100 μg/ml SO_4^{-2}) and 1 ml $1M$ $BaCl_2$.
III. Precipitation by seeding reagent prepared from 1 drop of sulphate standard solution (100 μg/ml SO_4^{-2}) and 1 ml $0.25M$ $BaCl_2$ in 50% v/v ethanol.
IV. Precipitation by seeding reagent prepared by 5 drops of sulphate standard solution (100 μg/ml SO_4^{-2} in 30% v/v ethanol) and 1 ml $1M$ $BaCl_2$.

The value of these methods is more accurately compared on the basis of the following experiments:

Investigations into the reproducibility and rate of precipitation in the precipitation of sulphate in relatively high and relatively low concentration in 5% NaCl and 5% KNO_3 solution. The results of these tests are given in Table V.

Determination of the relationship between nephelometer value and sulphate concentration in precipitation in the test solutions named. The results are given in Figs. 1 and 2.

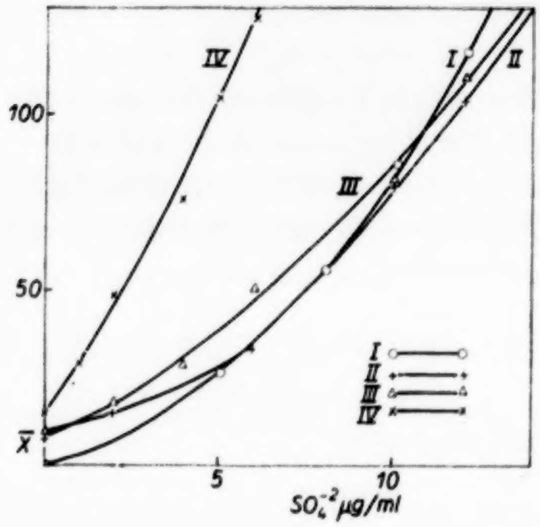

Fig. 1.
The relationship between sulphate concentration and nephelometer value in the detection of sulphate in 5% NaCl solution using methods I, II, III and IV (5 min, n = 10 or 20).

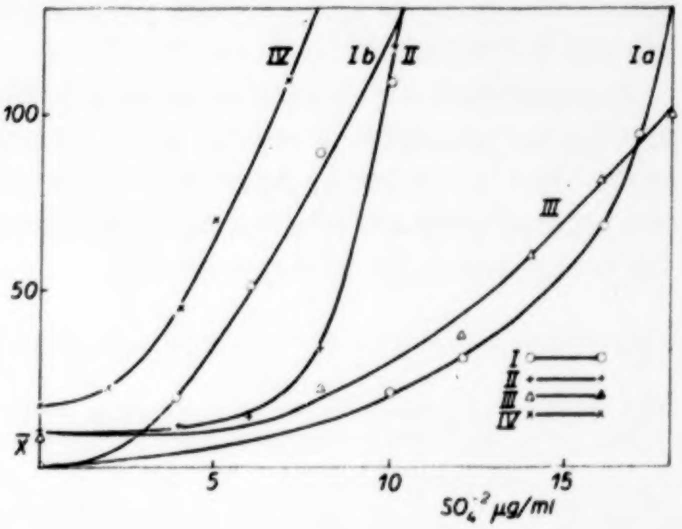

Fig. 2.
he relationship between sulphate concentration and nephelometer value in the detection of sulphate in 5% KNO_3 solution using methods I, II, III and IV (5 min, n = 10 or 20); (Ib: acidified with acetic acid).

Investigation of the detection of sulphate in other salt solutions, among which is sodium oxalate solution, which interferes with precipitation of barium sulphate to a marked degree. Table VI shows the results of these experiments.

TABLE V

THE PRECIPITATION OF BARIUM SULPHATE USING METHODS I-IV (SEE TEXT)

10 ml test solution + 1 ml $2M$ hydrochloric acid + reagent

Method	*Test solution* *Salt*	*SO_4^{-2} µg/ml*	*5 min (n = 20)* *x*	*s_{rel}*	*x (n = 5)* *5 min*	*10 min*	*30 min*
I	5% NaCl	2	16.9	7.8	17.8	18.9	19.5
I		12	118.0	4.1	122.3	125.7	128.7
II		2	14.7	15.1	14.5	15.6	18.8
II		12	102.9	6.8	103.5	105.8	106.0
III		4	29.1	11.3	29.9	39.4	49.4
III		12	102.1	7.2	105.5	104.2	102.8
IV		1	29.0	6.6	29.0	32.0	33.7
IV		5	104.7	6.9	106.4	107.2	105.3
I	5% KNO_3	10	20.7	14.5	19.7	39.7	113.5
I		17	95.1	12.8	95.1	> 130	> 130
I	[a]	4	20.7	34.4	15.1	27.8	50.9
I	[a]	10	108.6	6.1	106.8	120.7	126.2
II		6	14.2	14.0	14.7	20.8	56.3
II		10	119.0	7.4	119.0	> 130	> 130
III		8	21.9	7.7	20.8	30.6	51.4
III		18	100.5[b]	13.9	111.9	> 130	> 130
IV		2	21.9	5.4	21.3	26.7	36.7
IV		7	108.3	4.0	108.3	> 130	> 130

[a] 1 ml $2M$ acetic acid added instead of hydrochloric acid.
[b] n = 15.

The experiments in Table V show that Method IV gives the greatest sensitivity, rate of precipitation, and reproducibility. For precipitation in 5% NaCl solution, however, all methods must be considered satisfactory, as it must be remembered that when the opalescence is very weak only clear differences can be registered visually. Fig. 1 also shows that Method IV gives the greatest sensitivity when the measurements are made with a nephelometer. As the precipitated particles are very small the visibility of the precipitate is, however, not much greater than that obtained by the other methods. Method IV gives almost as great sensitivity in precipitation in KNO_3 solution as in NaCl solution (Fig. 2).

TABLE VI

DETECTION OF SULPHATE IN DIFFERENT SALT SOLUTIONS

After standing for 5 min. $n = 20$.

Salt	*Test solution*	*Method*	SO_4^{-2} *μg/ml*	$\bar{x}$	s_{rel}
Calcium chloride	10 ml 5% + 1 ml 2*M* HCl	I	10	124.8	4.4
		II	10	108.1	11.4
		III	5	96.7	4.2
		IV	4	80.6	3.2
Sodium acetate	8.5 ml 5% + 2.5 ml 2*M* HCl	I	8	102.7	6.9
		II	8	76.1	7.3
		III	8	89.6	5.7
		IV	6	103.3	5.7
Sodium phosphate	7.5 ml 5% + 3.5 ml 2*M* HCl	I	3	101.7	14.6
		II	3	114.0	11.5
		III	3	45.7	9.9
		IV	2	52.3	4.2
Sodium oxalate	8.5 ml 2% + 2.5 ml 2*M* HCl	I	20	58.3	14.4
		II	18	59.7	32.6
		III	20	65.8	8.3
		IV	10	56.1	3.3
Procaine-HCl	10 ml 2.5% + 1 ml 2*M* HCl[a]	I	5	80.4	6.2
		II	5	76.8	14.7
		III	5	75.9	8.0
		IV	4	95.6	4.0

[a] Blank value: $\bar{x} = 11.3$ (5 min, $n = 5$; method I).

The experiments in Table VI also credit Method IV with good reproducibility even in precipitation in sodium oxalate solution. Methods I and III give good results in most cases, and Method I has the advantage over Method IV that it is slightly easier to carry out, and that the visibility of the precipitate is greater, so that the opalescence is better suited to visual estimation. If the opalescence produced in Method IV is very weak it will be very much dependent on the lighting and method of observation whether it can be seen. This method is therefore most suitable in cases where a distinct opalescence must be produced in the test.

It must therefore be concluded from these experiments that Method I is usually preferable for use in practice. If it is desired to lay down a more definite limit for the content of sulphate in salts which retard the precipitation of $BaSO_4$ (nitrate, oxalate) Method IV may be used.

f. Standards

A standard for laying down the maximum permissible turbidity in a turbidimetric limit test should fulfil the following demands: Its turbidity must be reproducible, be similar to the turbidity which is normally produced in a purity test, if possible have good keeping qualities, and it should preferably be possible to produce it using the same reagents which are used in the test. A standard for use in detection of sulphate by Method I is best prepared in the following way: 1 ml $1M$ $BaCl_2$ is added to 1.00 ml sulphate standard solution (30 μg/ml SO_4^{-2} in 0.2M hydrochloric acid), and 1 min later 10 ml water are added: $\bar{x} = 81.0$, $s_{rel} = 6.1$ (5 min, $n = 20$). The turbidity decreases only slightly after standing for 30 min. If a sulphate standard solution without hydrochloric acid is used s_{rel} becomes larger.

A standard for use in the detection of sulphate by Method IV can be produced by 1.00 ml of the above-mentioned sulphate standard solution with 30% v/v ethanol which is precipitated by 1 ml $1M$ $BaCl_2$ and diluted by 10 ml water: $\bar{x} = 55.8$, $s_{rel} = 1.2$ (5 min, $n = 20$). The opalescence is practically unchanged after standing for 30 min.

Comparison of the test with the standard should be carried out in such a way that not only absorption but also scattering of light plays a part. This can be obtained by examining the liquids in test tubes at eye level in transparency against a black background (*e.g.* placed under a window).

2. LIMIT TEST FOR BARIUM

It has been shown earlier that barium can be detected in a test solution not containing salt, with good reproducibility, by precipitation with $1M$ H_2SO_4, but that salts reduce the sensitivity and reproducibility[16]. The reagent usually used for detection of barium in calcium salts, *i.e.* saturated $CaSO_4$ solution, gives very poor reproducibility. Better results are obtained with a seeding reagent produced by precipitation of a barium standard solution (100 μg/mg Ba^{+2}) with 0.1M H_2SO_4[17].

Out of the procedures which lead to improvement of the limit test for sulphate increasing the concentration of the reagent cannot be used in the limit test for barium when it must be possible to use the latter for testing for barium in calcium salts. The use of ethanol-containing reagents must be considered unfortunate because the mixture of ethanol and sulphuric acid does not keep; sulphuric acid cannot be replaced by sulphates as it has been shown before that in precipitation with Na_2SO_4 solution diminished reproducibility is obtained[16]. We have therefore investigated a third possibility: the use of a seeding reagent prepared by means of an ethanol-containing barium standard solution.

Preliminary experiments have shown that the amount of ethanol in the barium standard solution affects the precipitation of barium sulphate to a lesser extent in the test for barium than in that for sulphate. The best results are obtained with a barium standard solution with a relatively high ethanol concentration. For the experiments in Tables VII and VIII we have therefore used the barium-standard solution suggested by ILVER, JACKEROTT AND REIMERS[9] for the preparation of a standard for laying down the limit for the content of undissolved impurities in solutions of medicinal products (limit test for turbidity). This barium standard solution is prepared from a solution of 50 mg Ba^{+2} (as $BaCl_2$) in 1 ml water, which is diluted with 90% v/v ethanol to a total of 100 ml. Table VII shows that in the detection of barium in calcium chloride by means of a seeding reagent prepared from this barium solution greater rate of precipitation and reproducibility are obtained than that obtained with the reagent previously suggested. On the other hand the spreading of the results is somewhat larger in the detection of barium in salt-free solution. This is due to the fact that in a few experiments barium sulphate precipitates as finer crystals (the suspension turns a bluish colour) than is the case in the majority of the experiments. This is a much rarer occurrence in precipitation in calcium chloride solution. The differences between the visibility of the turbidities are less than the differences between the nephelometer values. These differences, therefore, do not render the method unusable.

TABLE VII

THE PRECIPITATION OF BARIUM SULPHATE BY SULPHURIC ACID SEEDING REAGENTS

10 ml test solution + seeding reagent prepared from barium standard solution + 1 ml 0.1 *M* H_2SO_4. $n = 20$.

Test solution		*Standard solution*			*5 min*		*10 min*	*30 min*
Salt	*Ba^{+2} µg/ml*	*Ba^{+2} µg/ml*	*Ethanol % v/v*	*Volume*	$\bar{x}$	s_{rel}	$\bar{x}$	$\bar{x}$
Absent	5	100	0	1 drop[a]	78.1	13.8	83.4	79.8
	10	500	89	0.14 ml[b]	65.1	13.0	69.7	70.2
5% $CaCl_2 \cdot 6H_2O$	5	100	0	1 drop	16.8	11.1	18.8	24.8
	10	,,	,,	,,	27.8	37.3	36.5	61.1
	20	,,	,,	,,	116.4	25.0		
	10	500	89	0.14 ml	39.9	4.8	41.3	42.8
	20	,,	,,	,,	100.1	2.9		

Blank values (seeding reagent + 10 ml water):

[a] $\bar{x} = 11.3$ (5 min, $n = 5$).

[b] $\bar{x} = 6.7$ (5 min, $n = 5$).

It must be added that the following changes in the experimental conditions do not raise the reproducibility: allowing the seeding reagent to stand for a longer period before addition of the test solution; the addition of a little ethanol to the measured quantity of ethanol-containing barium standard solution before the addition of 0.1 *M* H_2SO_4; the addition of ethanol to the test solution; and a longer period of standing after precipitation.

Table VIII shows some results of investigation into the detection of barium in solutions of different salts by means of the seeding reagents prepared from ethanol-containing barium standard solution. As a number of salts used in these experiments contain traces of barium the following procedure is used: a blank value is determined as the mean value of the nephelometer values for mixtures of test solution (T) and seeding reagent (R). This blank value is due to the influence of barium sulphate which comes from the seeding reagent and from the barium content of the salts. The blank value is shown in Table VIII: $\bar{x}_a$.

$BaCl_2$ (10 µg Ba^{+2} per ml) is added to another part of the test solution, and $\bar{x}$ is determined (shown as $\bar{x}_b$). As a measure of reproducibility s_{rel} is determined, and $\bar{x}_b - \bar{x}_a$ as a measure of sensitivity. This last difference is, however, not an exact measure of the turbidity which is produced by the quantity of $BaCl_2$ added to the test solutions, because the nephelometer value, as shown in Fig. 3, is not exactly proportional to the barium ion concentration.

TABLE VIII

DETECTION OF BARIUM IN DIFFERENT SALT SOLUTIONS

Seeding reagent: 6 drops of barium standard solution (500 µg/ml Ba^{+2} in 89% v/v ethanol) + 1 ml 0.1*M* sulphuric acid. 10 ml test solution (T) + seeding reagent (R)[a]. After standing for 5 min. $n = 20$.

Salt	*Test solution (T)*	*T + R*	*T + R (10 µg/ml Ba+2 added)*		$x_b - x_a$
		x_a	x_b	s_{rel}	
Calcium acetate	5%	13.8	40.6	3.5	26.8
Calcium chloride	5%[b]	7.3	38.8	6.5	31.5
	5%[c]		38.9	4.1	
	5%[d]		36.9	5.8	
Calcium gluconate	5%	16.5	40.7	1.1	24.2
	2%	17.1	57.1	5.2	40.0
Calcium lactate	5%	9.1	45.9	14.7	36.8
	2%	5.8	62.2	5.1	56.4
Calcium levulate	10%	31.2	61.9	5.0	30.7
	5%	11.8	58.8	4.3	47.0
Calcium mandelate	2% in ca. 0.8*M* CH_3COOH	19.3	66.2	3.7	46.9
Calcium phosphate	5% in ca. 0.7*M* HCl	11.6	37.4	5.9	25.8
	2% in ca. 0.3*M* HCl	12.1	42.7	6.2	30.6
Sodium chloride	5%	8.4	46.1	11.6	37.7
	2%	6.5	57.3	7.0	50.8
Potassium nitrate	5%	11.8	47.0	5.2	35.2

[a] Blank value (seeding reagent + 10 ml water): $\bar{x} = 10.6$ (5 min, $n = 10$).
[b] Analyst A.
[c] Analyst B.
[d] Analyst C.

Table VIII shows that barium is precipitated with good reproducibility in nearly all salt solutions, and that the sensitivity varies slightly. The rate of precipitation is great in all cases, although slightly reduced in the most concentrated salt solutions.

The following mixture may be used as a standard for turbidity: 1 ml 0.1*M* H_2SO_4 is added to 1.0 ml of the barium standard solution concerned, the mixture is shaken, and after 1 min is diluted with 10 ml water. This standard has a reproducible turbidity: $\bar{x} = 46.2$, $s_{rel} = 5.8$ (5 min, $n = 20$). The turbidity remains unchanged for at least 20 min.

3. LIMIT TEST FOR CALCIUM

In previous papers it has been shown that tests for calcium carried out by means of precipitation with 0.25*M* ammonium oxalate give very poorly reproducible turbidities, but that better results can be obtained by means of a seeding reagent and by precipitation at approx. 100° [1].

Of the procedures which lead to improvement in the limit test for sulphate, increasing the concentration of reagent and the preparation of seeding reagent by means of ethanol-containing reagent cannot be used in this case either, because 0.25*M* ammonium oxalate is almost saturated and causes precipitation on addition of ethanol. We have therefore investigated the effect of the ethanol content in the calcium standard solution used in the preparation of the seeding reagent, and in the test solution.

A series of experiments has shown that the ethanol content in the calcium standard solution raises the rate of precipitation, the sensitivity and the reproducibility. As examples of this can be mentioned that experiments with 5% NaCl solution with 4 μg/ml Ca^{+2} have given the following results (5 min, $n = 20$):

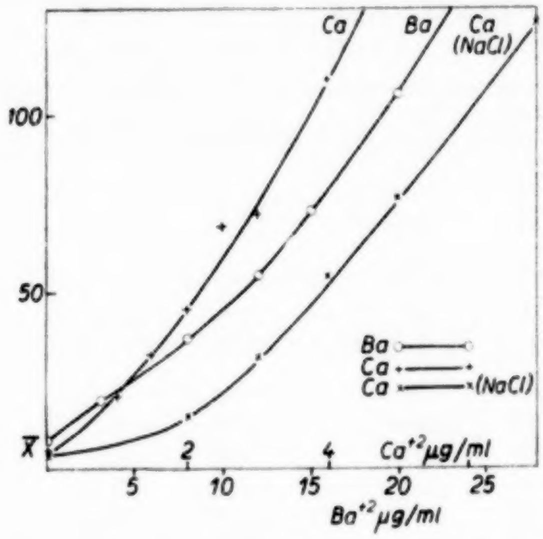

Fig. 3. The relationship between the concentrations of Ba^{+2} or Ca^{+2} and the nephelometer value in the detection of barium in 5% $CaCl_2$ solution and in the detection of calcium in salt-free solution and in 5% NaCl solution (5 min, $n = 10$ or 20).

0 % v/v ethanol: $x = 25.7$, $s_{rel} = 44.9$
Approx. 30 % v/v ethanol: $x = 76.7$, $s_{rel} = 7.0$
Approx. 60 % v/v ethanol: $x = 64.9$, $s_{rel} = 5.8$
Approx. 90 % v/v ethanol: $x = 73.7$, $s_{rel} = 5.8$

The precipitated calcium oxalate becomes finer with increase in ethanol content. However, with approx. 90% v/v ethanol the crystals are no finer than that the opalescence is well suited to visual assessment. As this ethanol concentration gave the best reproducibility in the preliminary experiments it has been chosen for use in the following experiments. The calcium standard solution used for these is prepared in the following way: to 10.0 ml $CaCl_2$ solution with 1.00 mg Ca^{+2} per ml ethanol 99% v/v is added to a total of 100 ml.

Table IX comprises the correlated results of experiments carried out partly by means of the earlier suggested seeding reagent (A), and partly by the seeding reagent prepared from an ethanol-containing calcium standard solution (B). It can be seen that heating to 100° raises the sensitivity of precipitation with reagent A, but that the reproducibility is unsatisfactory, especially in precipitation in NaCl solution. On the other hand reagent B gives a satisfactory reproducibility in all cases in that it must be remembered that even if s_{rel} is somewhat raised in experiments using very small calcium ion concentrations this is of no practical significance, as the turbidity is so weak that only a distinct difference can be observed.

Reproducibility, sensitivity, and rate of precipitation are further increased by the addition of ethanol to the test solution. However, as this means that the crystals of the precipitate become so small that the visibility of the opalescence is somewhat

TABLE IX

THE PRECIPITATION OF CALCIUM OXALATE WITH AMMONIUM OXALATE SEEDING REAGENTS

Reagent A: 2 drops of calcium standard solution (100 μg/ml Ca^{+2}) + 1 ml 0.25*M* ammonium oxalate.
Reagent B: 4 drops of calcium standard solution (100 μg/ml Ca^{+2} in 89% v/v ethanol) are added to 1 ml 0.25*M* ammonium oxalate.
10 ml test solution + reagent. $n = 20$ unless otherwise stated.

Test solution *Substance*	*Ca^{+2} μg/ml*	*Reagent*	*Temperature °C*	*5 min*		*10 min*		*30 min*
				$\bar{x}$	s_{rel}	$\bar{x}$	s_{rel}	$\bar{x}$
Absent	2	A	100[a]			56.9	16.4	66.7[e]
	4	A	20[b]	75.8	14.3	99.0[e]		118.2[e]
2% NaCl	2	A	100			22.8	36.3	36.8
5% NaCl	4	A	20	25.7	44.9	35.1[e]		53.9[e]
Absent	1	B[c]	20	20.4	8.7	23.4[e]		33.6[e]
	2	B	20	45.3	6.7	55.2[e]		60.5[e]
	3	B	20	71.6	4.0	79.9[e]		86.3[e]
	3[f]	B	20	87.4	2.9	87.9[e]		86.3[e]
	3[g]	B	20	99.1	3.0	96.4[e]		93.9[e]
	3[h]	B	20	101.5	3.3	99.6[e]		94.5[e]
5% NaCl	2	B[d]	20	14.8	9.6	22.1[e]		30.0[e]
	4	B	20	54.9	4.3	60.3[e]		59.0[e]
	6	B	20	89.7	5.3			84.0
	3[f]	B	20	60.2	1.9	62.3[e]		61.0[e]
	3[g]	B	20	83.1	3.0	83.1[e]		81.2[e]
	3[h]	B	20	105.7	2.8	103.9[e]		104.7[e]
0.2*M* NH_3	3	B	20	97.8	11.3	116.9[e]		123.6[e]
0.2*M* CH_3COOH	3	B	20	93.8	6.7	110.7[e]		114.4[e]

Blank values (seeding reagent + 10 ml water):
[a] $\bar{x} = 8.6$ (10 min, $n = 20$)
[b] $\bar{x} = 12.7$ (5 min, $n = 5$)
[c] $\bar{x} = 8.1$ (5 min, $n = 20$)
[d] $\bar{x} = 4.4$ (5 min, $n = 10$)
[e] $n = 10$
[f] 5% v/v ethanol
[g] 10% v/v ethanol
[h] 20% v/v ethanol

diminished, this possibility of improving the results should only be used in cases where adequate reproducibility cannot be obtained in any other way.

It is a wellknown fact that ammonia increases the sensitivity and that acetic acid diminishes the sensitivity in the detection of calcium as calcium oxalate. Table IX shows that 0.2*M* ammonia and 0.2*M* acetic acid do not alter the sensitivity to any great extent, when precipitation is carried out by means of the ethanol-containing seeding reagent.

Of the experiments carried out concerning the importance of different experimental conditions the following should be mentioned. The results are independent of the question whether the mixture of reagent and test solution is shaken or not. The reproducibility seems to be somewhat greater when the seeding reagent is prepared as stated in Table IX, than when the ammonium oxalate solution is poured over the calcium standard solution. The significance of temperature is shown in the following experiments: precipitation in a test solution containing 5% NaCl and 4 μg/ml Ca^{+2} at approx. 20°: $\bar{x} = 65.7$ (5 min) and 73.8 (10 min), at approx. 30°: $\bar{x} = 47.6$ (5 min) and 49.7 (10 min) ($n = 5$).

The results of experiments concerning the relationship between calcium ion concentration and nephelometer value are reproduced in Fig. 3.

It is known[1,18] that certain substances which form a complex with calcium, *e.g.* tartaric acid and citric acid, reduce the sensitivity and reproducibility of the limit test for calcium. In Table X the results of experiments concerning the detection of calcium in solutions of these and other substances are given. Good results in the detection of calcium in KNO_3, Na_2SO_4 and sugar have been obtained. The sensitivity and reproducibility in the detection of calcium in citric acid and tartaric acid can be raised by the use of ethanol-containing test solutions.

TABLE X

DETECTION OF CALCIUM IN SOLUTIONS OF DIFFERENT SUBSTANCES

10 ml test solution + seeding reagent (reagent B, Table IX). After standing for 5 min. $n = 20$.

Test solution					
Substance	*Concentration*	*Ca^{+2} µg/ml*	*Ethanol %v/v*	$\bar{x}$	s_{rel}
Potassium nitrate	5%	4	0	92.2	4.8
Sodium sulphate	5%	3	0	46.3	5.4
Citric acid	5%	10	0	21.9	20.0
		10	5	34.5[a]	
		5	10	24.8	10.7
Tartaric acid	5%	10	5	4.2[a]	
		20	10	44.4	7.7
		50	10	88.8	7.7
Sucrose	5%	2	0	66.5	2.5

[a] $n = 10$

A mixture of the calcium standard solution and $0.25\,M$ ammonium oxalate cannot be used as a standard for turbidity because the visibility of the precipitate is too small on account of the large ethanol content of the mixture. The standard must consequently be prepared by precipitation of a solution containing a known amount of calcium by means of the seeding reagent. This can be done by using the ethanol-containing calcium standard solution as follows: 0.50 ml of the calcium standard solution is diluted with 10 ml water, and the mixture is precipitated by means of the seeding reagent. In the case of such a standard — although prepared from 0.30 ml calcium standard solution — $\bar{x} = 100.0$, $s_{rel} = 3.9$ (5 min, $n = 20$). The turbidity changes slightly on standing (10 min: $\bar{x} = 107.2$, 30 min: $\bar{x} = 108.4$).

4. LIMIT TEST FOR SULPHATE, BARIUM AND CALCIUM

In conclusion of the experiments carried out the following limit tests for sulphate, barium and calcium are suggested, by means of which limits for these impurities can be laid down with the required reproducibility[19].

Sulphate

1 ml 1*M* $BaCl_2$ is added to 10 ml test solution, and the mixture is then shaken vigorously for 10 sec. The turbidity is assessed after standing for 5 min. Standard: 1 ml 1*M* $BaCl_2$ is added to 1.0 ml sulphate standard solution (30 μg/ml SO_4^{-2} in 0.2*M* hydrochloric acid), shaken, and after the elapse of 1 min is mixed with 10 ml water.

If it is desired to lay down a limit for the content of sulphate in salts which retard the precipitation of $BaSO_4$ (nitrate, oxalate) with greater certainty than is offered by the method mentioned, the test is carried out as follows: 1 ml 1*M* $BaCl_2$ is added to 5 drops (measured by means of a standard medicine dropper) of sulphate standard solution (100 μg/ml SO_4^{-2} in 30% v/v ethanol). After shaking and after 1 min standing a mixture of 10 ml test solution (neutral or acid) and 1 ml 2*M* hydrochloric acid is added. The turbidity is assessed after standing for 5 min. Standard: 1.00 ml of the sulphate standard solution mentioned is mixed with 1 ml 1*M* $BaCl_2$ and after 1 min diluted with 10 ml water.

Barium

1 ml 0.1*M* H_2SO_4 is added to 6 drops (measured by means of a standard dropper) of barium standard solution (500 μg/ml Ba^{+2} in 89% v/v ethanol). After standing for 1 min 10 ml test solution is added, and the whole is shaken vigorously for 10 sec. The turbidity is assessed after standing for 5 min. Standard: 1 ml 0.1*M* H_2SO_4 is added to 1.00 ml of the barium standard solution mentioned, and after shaking and standing for 1 min it is diluted with 10 ml water.

Detection of barium in a test solution not containing salt can be carried out with 1*M* H_2SO_4 (10 ml test solution and 1 ml reagent).

Calcium

4 drops (measured by means of a standard dropper) of calcium standard solution (100 μg/ml Ca^{+2} in 89% v/v ethanol) are added to 1 ml 0.25*M* ammonium oxalate, and after shaking and standing for 1 min 10 ml test solution (neutral, weakly ammoniacal, or slightly acidified by acetic acid) is mixed with it. The turbidity is assessed after standing for 5 min. Standard: 0.50 ml of the calcium standard solution mentioned is diluted with 10 ml water and precipitated with the seeding reagent; it is used after standing for 5 min. For detection of calcium in citric acid and tartaric acid a test solution with 10% v/v ethanol is used.

The above-mentioned standards for turbidity are used if a positive reaction for the impurity is to be allowed, the concentration of the test solution being chosen in such a way that the turbidity produced is at the most the same as in the standard. If reactions for impurities must not occur, blanks (reagents — possibly seeding reagents — to which water is added) are used as standards.

ACKNOWLEDGEMENT

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SUMMARY

An attempt is made to improve earlier suggested limit tests for sulphate, barium and calcium, among other things on the basis of older and newer investigations into the crystallization of barely soluble substances.

Limit tests with satisfactory reproducibility have been worked out for the impurities in question. The procedures which lead to the improved results are: increasing the concentration of the reagent (sulphate) and precipitation with seeding reagents prepared from ethanol-containing standard solutions (sulphate, barium, calcium).

Prescriptions for standards having reproducible turbidity have been worked out.

RÉSUMÉ

Une étude a été effectuée en vue d'améliorer les essais de limites décrits précédemment pour les sulfate, baryum et calcium, entre autres, en se basant sur des recherches plus anciennes et plus récentes sur la cristallisation de substances très peu solubles. Des essais de limite ont été effectués pour les impuretés en question avec une reproductibilité satisfaisante. Les procédés permettant d'obtenir de meilleurs résultats sont: augmentation de la concentration du réactif (sulfate) et précipitation avec des réactifs d'amorçage préparés au moyen d'une solution de référence renfermant de l'éthanol (sulfate, baryum, calcium). Des indications sont données pour préparer des étalons présentant un trouble reproductible.

ZUSAMMENFASSUNG

In dieser Arbeit wird ein Versuch gemacht, um früher beschriebene Grenzteste für Sulfat, Barium und Calcium zu verbessern, unter anderem auf Grund älterer und neuerer Untersuchungen über Kristallisation sehr schwer löslicher Substanzen. Grenzteste mit befriedigender Reproduzierbarkeit wurden für die betreffenden Verunreinigungen ausgearbeitet. Man erhält die besseren Resultate durch Erhöhung der Reagenzkonzentration (Sulfat) und durch Impfen mit Reagenzien, erhalten aus äthanolhaltigen Standardlösungen (Sulfat, Barium, Calcium). Es wurden Vorschriften für die Herstellung von Standardlösungen mit reproduzierbarer Trübung ausgearbeitet.

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DETERMINATION AND SEPARATION OF COPPER IN METALLURGICAL PRODUCTS

by

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One of the most useful separations of copper is the precipitation as cuprous thiocyanate[1], after reduction with ammonium bisulfite in a weakly acid solution[2].

In attempts to overcome some of the disadvantages of this method the author has found that ascorbic acid can be used with potassium thiocyanate for the precipitation of copper as cuprous thiocyanate according to the reaction:

$$2\ Cu^{+2}+C_6H_8O_6+2\ SCN^- = 2\ CuSCN+C_6H_6O_6+2\ H^+$$

Furthermore ascorbic acid has been found to eliminate the interference of lead, bismuth and cadmium so that the isolation of copper from solutions containing these ions may be accomplished by potassium thiocyanate[3,4].

The proposed method was found to offer advantages over the electrolytic method. The very valuable electrolytic process for copper will not work in the presence of cadmium and bismuth. Apart from the effective determination of copper in the presence of lead, bismuth and cadmium, the presence of phosphates, zinc, antimony, iron, manganese, nickel and chromium does not affect the copper determination, so that the method can also be applied in a number of alloys.

In silver alloys, silver and copper are conveniently determined on the same sample, since ascorbic acid is effective for the reduction of silver. After silver is first removed by ascorbic acid, copper is precipitated in the presence of the other ions by addition of potassium thiocyanate.

In bronzes and in alloys containing silicon, copper was determined after the elimination of tin and silicon.

Standard samples issued by the National Bureau of Standards, British Chemical Standards and routine laboratory samples were analysed for the applicability of the method.

EXPERIMENTAL

The accuracy of the method was tested by dissolving accurately weighed pure copper (J. M. 30 Matthey copper rod) in nitric acid. After complete solution, addition of standard solutions of lead, bismuth, cadmium and zinc was made.

The solution was finally diluted with water and copper was precipitated at room temperature.

Solutions

Ascorbic acid 3 g per cent and 11 g per cent in water. Potassium thiocyanate 10 per cent. Standard solutions of lead, cadmium and bismuth were prepared by dissolving weighed amounts of the pure nitric salts in known volume of water or dilute nitric acid.

Procedure in absence of bismuth

Take the appropriate weight of copper in a 250 ml beaker and dissolve in 3 ml of $6N$ nitric acid. Heat over a steam bath to expel oxides of nitrogen and dilute to 200 ml with water. Pour in, with stirring, 8.5 ml of ascorbic solution 3% and then add slowly 2 ml of potassium thiocyanate solution. Keep stirring for 5 minutes and let stand for 30 minutes. Filter through a [illegible]ex sintered-glass crucible F (fine porosity) that has been brought to constant weight at 120 [illegible]. Wash with 150-200 ml of water, dry at 120°C and weigh as cuprous thiocyanate.

Procedure in presence of bismuth

Dissolve the appropriate weight of copper in 10 ml of $6N$ nitric acid and heat over a steam bath to expel oxides of nitrogen. Dilute after the addition of bismuth ion to 150 ml with water. Pour in with stirring 8.5 ml of ascorbic acid solution 3% and then add slowly 2 ml of potassium thiocyanate solution. Keep stirring for 5 minutes, let stand 15 minutes and filter through a pyrex sintered-glass crucible F. Wash with 150 ml nitric acid solution (1 ml HNO_3 $15.7N + 49$ ml H_2O) and then with 150 ml of water.

Procedure for silver alloys

Take 0.2 g of the alloy in a 150 ml beaker, dissolve in 3 ml of $6N$ nitric acid and heat gently to expel oxides of nitrogen. Dilute to 20 ml with water heat the solution to 90-100°C and pour in, with stirring, 8.5 ml of ascorbic acid solution 3%. Continue the heating for 15 minutes and promptly filter through a porcelain filter crucible. Wash the precipitate with hot water, ignite and weigh as Ag. Dilute the filtrate and washings from the silver determination to 200 ml, cool and pour in with stirring 2 ml of potassium thiocyanate solution. Keep stirring for 5 minutes and let stand 30 minutes. Filter through a sintered-glass crucible F, wash with 200 ml of water and dry at 120°C.

Procedure for bronzes

Take 0.25 g of the alloy in a covered 150 ml beaker and dissolve in 10 ml of nitric acid (1 : 1). Heat over a steam bath for 45 minutes, remove and rinse the cover glass and evaporate to 5 ml. Dilute to 50 ml with water, digest at 80-90°C for 15 minutes and filter through a fine grained ashless filter paper. Wash the precipitate of stannic acid with 150 ml of nitric acid 1 : 20, reserve the filtrate and washings in a 200 ml volumetric flask an dilute with water to the mark. Withdraw 40 ml into a 250 ml beaker, dilute to 200 ml and precipitate copper at room temperature with 8.5 ml of ascorbic acid 3% and 2 ml of potassium thiocyanate. After 30 minutes filter through a sintered-glass crucible F, wash with 50 ml of nitric acid (1 ml HNO_3 $15.7N + 49$ ml H_2O) and then with 150 ml of water. Dry at 120°C to constant weight.

Procedure for cast iron

Take 0.5 g of the alloy in a covered 250 ml beaker and treat with 50 ml of diluted sulfuric acid (1 :4). Boil vigorously, as the particles tend to become coated with the gelatinous silica, and when the reaction ceases add carefully 5 ml of 6*N* nitric acid. Heat until carbides are decomposed and oxides of nitrogen are expelled. Remove and rinse the cover glass. Dilute the solution thus obtained to 100 ml heat, let stand 5 minutes and then filter through a rapid ashless filter paper in a 250 ml volumetric flask. Wash the residue and the filter with 100 ml of hot water to which 2-3 drops of conc. sulfuric acid have been added and dilute to the mark.

Withdraw 50 ml into a 250 ml beaker, dilute to 150 ml, pour in with stirring 20 ml of 3% ascorbic acid solution and then add slowly 2 ml potassium thiocyanate. Keep stirring for 5 minutes and let stand 30 minutes. Filter through a sintered-glass crucible F, wash with 200 ml of water and dry to constant weight at 120°C.

Procedure for steels

Take 1 g of the steel (copper content 0.1-0.2 per cent) in a covered beaker and treat with 20 ml of diluted sulfuric acid 1 :4. Simmer to dissolve and when the reaction ceases add carefully 5 ml of 6*N* nitric acid. Heat (about 30 min) until carbides are decomposed and oxides of nitrogen are expelled. Remove and rinse the cover glass. Dilute the solution thus obtained to 100 ml heat and let stand 3 minutes. Filter the residue through a dense filter paper (S.S.589 blue ribbon) in a 250 ml beaker. Wash the residue and the paper with 100 ml of hot water to which 2-3 drops of conc. sulfuric acid have been added.

Concentrate the filtrate to about 200 ml if the volume is greater than this, cool to room temperature, pour in with stirring 20 ml of ascorbic acid solution 11% and then add slowly 2 ml of potassium thiocyanate solution. Keep stirring for 5 minutes and let stand 30 minutes. Filter through a sintered-glass crucible F, wash with 100-150 ml of water and dry to constant weight at 120°C.

RESULTS

A comparison of results obtained on synthetic samples and on a number of alloys is shown in Tables I and II from which it can be seen that the results agree satisfactorily.

TABLE I

DETERMINATION OF COPPER

Copper added g	*Other metal added* g	*Copper found* g
0.1004		0.1004
0.0992		0.0991
0.0388		0.0389
0.0295		0.0294
0.0131		0.0132
0.0098		0.0099
0.0408	Pb 0.0313	0.0409
0.0404	Bi 0.0285	0.0404
0.0406	Bi 0.0285	0.0406
0.0302	Cd 0.0387 + Zn 0.0312	0.0302

TABLE II

DETERMINATION OF COPPER IN ALLOYS

Type of alloy and certified values	*Weight of sample* g	*CuSCN found* g	*Cu found* %	*Ag found* %
One dime coin 1929: Ag 90, Cu 10	a) 0.2005	0.0387	10.08	90.0
	b) 0.2000	0.0385	10.05	90.0
	c) 0.2029	0.0390	10.04	89.98
B.C.S. Bronze "A" 183: Cu 85.5, Sn 9.96, Zn 1.86, Pb 1.83, P 0.25, Sb 0.24, Fe 0.07, Ni 0.04, As 0.06, O 0.43.	a) 0.2829	0.4625	85.43	
	b) 0.2520	0.4120	85.43	
	c) 0.2536	0.4150	85.51	
B.C.S. Ni-Cu-Cr Austenitic Cast Iron "L" No. 173: C 3.06, Si 2.26, Mn 1.01, S 0.031, P 0.119, Ni 13.45, Cr 3.97, Cu 4.73.	a) 0.4995	0.0454	4.75	
	b) 0.5015	0.0459	4.78	
	c) 0.5022	0.0458	4.76	
N.B.S. Chrom-Molybdenum-Aluminum (Nitralloy "G") Steel Standard Sample No. 106: C 0.342, Mn 0.481, P 0.021, S 0.019, Si 0.25, Cr 1.29, Mo 0.163, Al 1.06, Cu 0.141, Ni 0.131, V 0.008, As 0.009.	a) 1.0084	0.0030	0.155	
	b) 1.0030	0.0029	0.151	
	c) 0.9690	0.0029	0.156	

SUMMARY

Rivot's process for the separation and the determination of copper as cuprous thiocyanate has been modified. The modified method involves the reduction of cupric ion in nitric acid solution by ascorbic acid and makes the procedure practicable, since good results may be obtained with rapidity and ease. The method is applied to a wide variety of metallurgical products.

RÉSUMÉ

La méthode de Rivot pour la séparation et le dosage du cuivre à l'état de thiocyanate de cuivre(I) est modifiée; elle consiste à réduire le cuivre(II) par l'acide ascorbique, en solution acidifiée par l'acide nitrique. La méthode devient alors rapide et pratique; elle peut s'appliquer à une grande variété de produits métallurgiques.

ZUSAMMENFASSUNG

Das Verfahren von Rivot für die Trennung und die Bestimmung von Kupfer als Cuprorhodanid wurde in der Hinsicht abgeändert, dass die Reduktion der Kupfer(II)-ionen in salpetersaurer Lösung mittels Ascorbinsäure erfolgt. Dieses Verfahren ist dadurch vorteilhaft, dass die Bestimmung rasch und einfach durchgeführt werden kann. Es ist auf eine grosse Anzahl von metallurgischen Produkten anwendbar.

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SEPARATION OF URANIUM FROM VANADIUM BY ION EXCHANGE: WITH SPECIAL REFERENCE TO THE DETERMINATION OF SMALL AMOUNTS OF URANIUM

by

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Vanadium interferes with the determination of uranium by gravimetric and volumetric methods. The presence of vanadium also modifies the behaviour of uranium solutions towards sodium hydroxide by preventing precipitation or rendering it incomplete[1]. Even in the colorimetric determination of uranium by a number of reagents including sodium peroxide[2] and ammonium thiocyanate[3] the interference due to vanadium has been noted. Of the various methods described[4] for the separation of vanadium from uranium the cupferron method appears to be the best. However, this suffers from the disadvantage that large amounts of organic matter have to be destroyed before the separated vanadium and uranium can be estimated. In this paper an ion exchange method of separation is described which permits the separation of milligram quantities of uranium from large amounts of vanadium.

Because of its strong oxidizing property vanadium (VO_2^+ ion) reacts with many of the ion exchange resins in acid medium. No such difficulty is found in alkaline medium. But in such solutions uranium gets precipitated unless a complexing agent is present. Hence anion exchange in sodium carbonate solution appeared to be promising for the separation of vanadium and uranium as both are present as anions — VO_3^- and $[UO_2(CO_3)_3]^{-4}$ respectively. The difference in valency of the two ions can be taken advantage of in affecting a separation.

EXPERIMENTAL

Preliminary batch and column experiments showed that uranium as complex uranyl tricarbonate was strongly adsorbed by ion exchange resins while vanadium as vanadate (VO_3^-) was only moderately adsorbed. Moreover the adsorbed vanadium could be removed quantitatively by a 5-10% solution of sodium carbonate leaving uranium in the column. When vanadium was fed on to a column of anion exchanger (Amberlite IRA-400) in a 5-10% sodium carbonate solution, part of it passed through unadsorbed.

The separation of vanadium and uranium, therefore, involved passing a solution of the two, containing some excess sodium carbonate, through an anion exchanger column followed by elution of vanadium with sodium carbonate solution. Of many solutions tried as eluants for the adsorbed uranium sodium chloride was finally chosen.

Reagents

Standard vanadium and uranium solutions were prepared from AnalaR grade sodium metavanadate and uranyl nitrate.

Resin

The resin employed was pretreated as follows:
Commercial grade Amberlite IRA-400 (Cl^-) was sieved and the portion passing through British Standard Sieve 22 was taken and freed from fines by repeated washing with water, allowing the larger particles to settle and decanting off the fines. The resin was further purified by stirring it in a beaker alternatively with a large excess of 2*M* sodium hydroxide and hydrochloric acid.

After two such cycles it was transferred to a column, completely converted into the chloride form by passing excess of 2*M* sodium chloride and rinsed with distilled water till the effluent was free from chloride. It was then removed from the column, air-dried and stored.

Column

The columns used for the study were of the conventional type, 15 mm in internal diameter and about 20 cm high. 10 g of the air-dried resin was used for each column giving a bed depth of about 10 cm. The flow-rate of the sample solution and eluant was controlled by the stop cock of the dropping funnel which served as a reservoir.

Uranium determinations were made by the sodium hydroxide-sodium peroxide method, optical densities being measured with a Beckman model DU spectrophotometer at 420 mμ. When the amounts involved were more than 20 mg estimations were done gravimetrically.

Determinations of vanadium were done mostly by titration with ferrous ammonium sulphate.

Adsorption and recovery of vanadium

The elution characteristics of vanadium are shown in Fig. 1. 10% sodium carbonate passed at a rate of 100 ml/h could elute vanadium effectively; but the volume of eluant to be passed for complete elution of vanadium depended on the amount of vanadium adsorbed on the column. In order to reduce the time taken for the elution step it was necessary to carry out the adsorption step in such a way that the amount of vanadium adsorbed on the column was very small. This could be done by (i) increasing the free sodium carbonate concentration in the sample solution and (ii) increasing the rate at which the test solution was passed. Vanadium solutions containing up to a maximum of 250 mg V_2O_5 were diluted to 100 ml after addition of 10 g Na_2CO_3 and

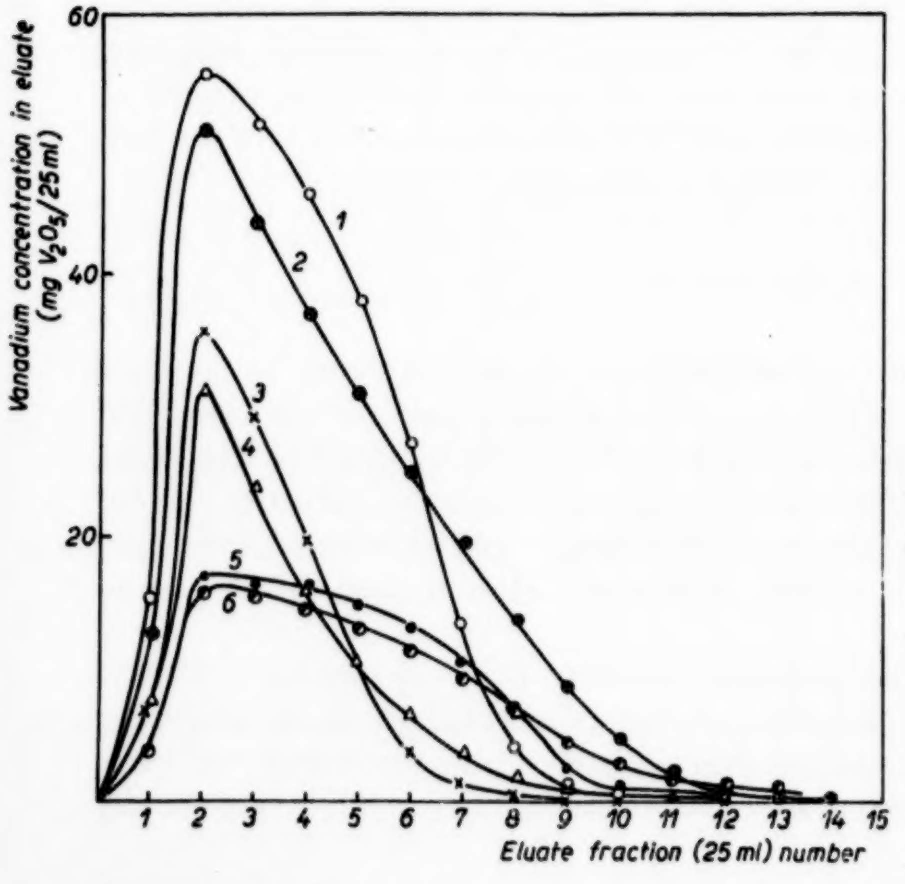

Fig. 1. Elution of vanadium with sodium carbonate

Curve No.	*Vanadium adsorbed on the column mg V_2O_5*	*Eluant*	*Rate of elution ml/h*
1	250	10% Na_2CO_3	100
2	250	,,	200
3	100	,,	100
4	100	,,	200
5	100	5% Na_2CO_3	100
6	100	,,	200

References p. 28.

passed through a column at a rate of 500 ml/h. Under these conditions most of the vanadium was found to be in the effluent. 200 ml of 10% sodium carbonate was found enough to elute quantitatively the adsorbed vanadium, the elution rate being 100 ml/h.

Adsorption and recovery of uranium

While the adsorption of vanadium was very poor from a solution containing 10 % free sodium carbonate (passed at a rate of 500 ml/h) it was found that uranium was quantitatively taken up by the column under the same conditions provided its concentration was not more than 50 mg per 100 ml. Even after a subsequent passage of a liter of 10 % sodium carbonate solution (at a rate of 100 ml/h) uranium was found to be still completely retained on the column. It was, however, quantitatively eluted by 5 % sodium chloride solution (containing 5 g/l sodium carbonate). For the subsequent colorimetric estimation of small amounts of uranium the eluate was concentrated to a suitable volume. There was no interference in the estimation due to the excess sodium chloride present.

Effect of other anions on the adsorption of vanadium and uranium

Though the presence of moderate amounts of chloride, nitrate and sulphate has no effect on the adsorption of vanadium, more than a few miligrams of chloride or nitrate was found to cause the leakage of uranium and hence should be eliminated; sulphate can, however, be tolerated up to 1-2 g SO_4^{-2} per 100 ml test solution. Therefore it is necessary to fume the test solution with H_2SO_4 (if it contains Cl^- or NO_3^-) and neutralize with sodium hydroxide before adding Na_2CO_3 and passing through the column.

Separation of vanadium and uranium

For testing the separation of small amounts of uranium from vanadium the following procedure was finally adopted:

To a mixture containing known amounts of vanadium and uranium and containing no free acid 10 g sodium carbonate was added and the volume made up to 100 ml. The maximum concentrations of vanadium and uranium were adjusted to be 250 mg V_2O_5 and 50 mg U_3O_8 respectively per 100 ml. This solution was passed through a column at a rate of 500 ml/h followed by a washing with 30 ml 10 % sodium carbonate at the same rate. Another 200 ml of 10 % sodium carbonate was passed at a rate of 100 ml/h to elute vanadium completely. The column was finally washed with 30 ml distilled water and the washings collected along with the effluent and the eluate and the vanadium content estimated volumetrically.

Uranium was then eluted by passing 150 ml of 5 % sodium chloride (containing 5 g Na_2CO_3/l) at a rate of 100 ml/h. The column was washed with 50 ml distilled water at 500 ml/h and the washings collected along with the eluate and uranium was determined. Results of several such separations are shown in Table I.

TABLE I

SEPARATION OF URANIUM AND VANADIUM

Expt. No.	*V_2O_5 taken* mg	*U_3O_8 taken* mg	*Volume of sample solution* ml	*V_2O_5 recovered* mg	*U_3O_8 recovered* mg
1	25	25	100	25.1	24.9
2	50	25	100	50	25.1
3	100	25	100	100	25.2
4	100	50	100	100	49.2
5	250	25	100	249.1	24.8
6	250	50	100	250	49.5
7	100	1	100	. . .	1.05
8	100	2	100	. . .	2.08
9	250	1	100	. . .	1.00
10	250	2	100	. . .	2.10
11	500	1	200*	. . .	1.00
12	1 g	1	400*	. . .	1.02

* Since the last two separations involved more than 250 mg V_2O_5, the sample solution was diluted to 200 and 400 ml respectively maintaining a sodium carbonate concentration of 10 g per 100 ml.

References p. 28.

For a second cycle of operation the column was regenerated by passing 250 ml of 5 % sodium chloride at 100 ml/h followed by rinsing with distilled water till the effluent was free from chloride.

The results show that 1 mg of U_3O_8 could be separated from as much as 1 g of V_2O_5 by following the details given in the procedure. When the uranium concentration in the sample was more than 50 mg U_3O_8 per 100 ml it was observed that under the given conditions of column operation part of it passed out in the effluent along with vanadium. Hence the sample solution should be suitably diluted before passing through the column.

The procedure described in this paper will be useful in the separation of large amounts of vanadium from uranium before the latter is estimated colorimetrically.

ACKNOWLEDGEMENT

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SUMMARY

An ion exchange method has been worked out for the separation of milligram quantities of uranium from large amounts of vanadium. A solution containing vanadium and uranium and excess sodium carbonate is passed through a column filled with an anion exchanger in the chloride form. All the uranium and part of the vanadium are adsorbed by the resin. The adsorbed vanadium is first eluted with 10 % sodium carbonate solution leaving uranium in the column. Uranium is then eluted with sodium chloride and estimated colorimetrically.

RÉSUMÉ

Une méthode par échange d'ions a été établie pour la séparation de quantités d'uranium de l'ordre du milligramme d'avec de fortes teneurs de vanadium. Une solution renfermant le vanadium et l'uranium, et un excès de carbonate de sodium, est passée à travers une colonne remplie d'un échangeur d'anions sous forme de chlorure. Tout l'uranium et une partie du vanadium sont adsorbés par la résine. Le vanadium adsorbé est d'abord élué avec une solution de carbonate de sodium à 10 %, tandis que l'uranium reste dans la colonne. Ce dernier est ensuite élué avec une solution de chlorure de sodium et dosé colorimétriquement.

ZUSAMMENFASSUNG

Eine Ionenaustausch-Methode wird beschrieben, mit deren Hilfe kleine Mengen an Uran (von der Ordnung des Milligramms) von grossen Mengen an Vanadin getrennt werden können. Eine Lösung welche Vanadin, Uran und einen Überschuss an Natriumcarbonat enthält wird auf eine Anionenaustauschersäule in der Chloridform gegossen. Das gesammte Uran und ein Teil des Vanadins werden von dem Harz adsorbiert. Nun wird das adsorbierte Vanadin mit einer 10 %-igen Natriumcarbonatlösung eluiert wobei das Uran in der Säule bleibt. Dieses wird dann mit Natriumchlorid eluiert und kolorimetrisch bestimmt.

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QUANTITATIVE ANALYSIS WITH THERMAL CONDUCTIVITY DETECTION IN GAS-LIQUID CHROMATOGRAPHY

by

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INTRODUCTION

In gas chromatography the presence of a component in the column effluent is sensed and recorded by some system of detection. Several such detectors, each possessing certain merits and disadvantages, have been proposed. They can be divided into two classes. The first produces a record of the integrated value of some quantity measured by the instrument and may be termed the "integral" type. The second class ("differential" detectors) records a momentary property of the effluent as it passes through the detector, and thus reverts to a basic indication when pure carrier gas is flowing through it. The record of the first type shows a series of steps, that of the second a number of peaks on a base line. The two types of record are, in principle, interconvertible by differentiation or integration.

An equally important difference between detectors lies in the nature of the signal that they produce. If this signal stands in a linear relation to the amount (or concentration) of an eluted component and depends on some simple molecular parameter characterizing it, the quantitative interpretation of a chromatogram is a relatively simple matter. The integral detection methods that have been employed have all been so chosen that this condition is fulfilled. JAMES AND MARTIN[1], in their pioneering work on the quantitative estimation of volatile fatty acids and amines by G.L.C., titrated the column effluent by means of an automatic device. The "signal" of this detector stands in alinear relationship to the amount of the component; the molecular parameter is here its acidity or alkalinity. Other integral methods of detection have involved the measurement of volume increments at constant pressure[2] or pressure increments at constant volume[3] (both after removal of the carbon dioxide employed as carrier gas), or the measurement of the electric conductivity of a suitable electrolyte in which the components of the sample are collected[4]. With these methods, again, calculation of the quantitative composition is quite straightforward for the same reasons.

The systems of detection mentioned above have, however, but a limited field of application. On this account investigators employing G.L.C. have latterly favoured the use of differential systems, several of which are more generally applicable and independent of the nature of the materials to be separated.

Intrinsically there is no reason why the signal of a differential detector, also, should not fulfil the conditions required for direct quantitative interpretation, *viz.* linearity with respect to concentration and dependence on some simple molecular parameter. Differential systems closely conforming to these requirements have been devised*. MARTIN's "gas balance"[6] records the density of the column effluent; radiological detection[5,7], which is based on the measurement of ionization currents produced on irradiation, gives a signal proportional to the concentration and ionization cross section of component molecules. Both of these parameters can be used for the purpose of direct quantitative calculation.

The differential detector that has been most intensively developed and is at present most widely employed is the katharometer, or thermal conductivity cell. This detector (though possessing several important practical advantages) does not conform to the demands enumerated above; the same applies to several other differential types that have been proposed. The signal of the katharometer is not strictly proportional to the concentration of the component in the issuing gas; furthermore, it is not related to a simple molecular parameter of the component and carrier gas. In principle, therefore, such a detector requires a process of *calibration*; so as to establish the response for a particular component and for the concentration in which it is present.

This paper will deal with the factors affecting the signal of the thermal conductivity cell and with the methods employed for its calibration.

FACTORS INFLUENCING THE RESPONSE OF THE KATHAROMETER

As stated above, there is as a rule not a linear relation between the response of a katharometer and the concentration of the component in the carrier gas. Both positive and negative deviations from linearity can occur, as illustrated in Fig. 1, which represents the thermal conductivities (λ) of mixtures containing various percentages of *iso*butane or carbon dioxide in nitrogen. It will be seen that though *iso*butane and CO_2, in 100% concentration, differ but little in thermal conductivity, the curves of mixtures with nitrogen are widely different. Published values of λ for pure compounds are hence of very little use in these cases.

In G.L.C. the concentration of a component in the carrier gas will normally not exceed, say, 10%. The first parts of the curves for CO_2 and *iso*butane in nitrogen, between 0 and 10%, are both almost straight. If this part of the curve is extrapolated to 100% concentration by a straight line (dotted in the figure), an "effective" thermal conductivity (λ') is found, the value that must be used for interpolation between 0 and 10%. The figures for λ', in the case of CO_2 and *iso*butane, differ by a factor of almost 2.

In other cases, however, even the first part of the curve is not reasonably straight. VAN DE CRAATS[8] has shown that the curve for acetylene in nitrogen, between 0 and 10%, has a maximum, as indicated in Fig. 2. Owing to this shape of thermal conductivity curve, the elution diagram for C_2H_2 in N_2 may consist of a peak standing in depressions, as illustrated in Fig. 3.

Furthermore, the relative change in thermal conductivity (*viz.* the slope of the first part of the curve referred to above), is a function of temperature. If the thermal conductivities of component and carrier gas do not differ much, it may occur in practice that this slope is positive at one temperature and negative at another.

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* For a review of detection systems, see BOER[7].

In the foregoing the carrier gas considered has been nitrogen, which is still largely used for various good reasons. Hydrogen and helium have very much higher thermal conductivities; the non-linearities discussed are much smaller for these carrier gases, though they cannot be neglected for the most accurate results. The relative change in thermal conductivity is then also much less dependent on the nature of the component; though the effect is still present, the slope of the curve with these carrier gases may sometimes be assumed to be constant for compounds of similar type, particularly if the highest accuracy is not essential.

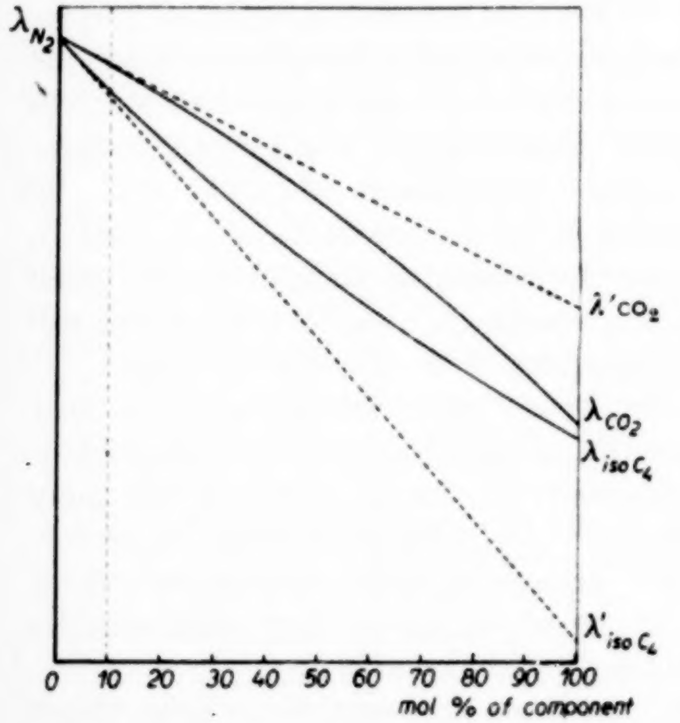

Fig. 1. Thermal conductivity of gas mixtures. (N_2-CO_2 and N_2-*Iso*butane)
λ = True thermal conductivity
λ' = Apparent thermal conductivity.

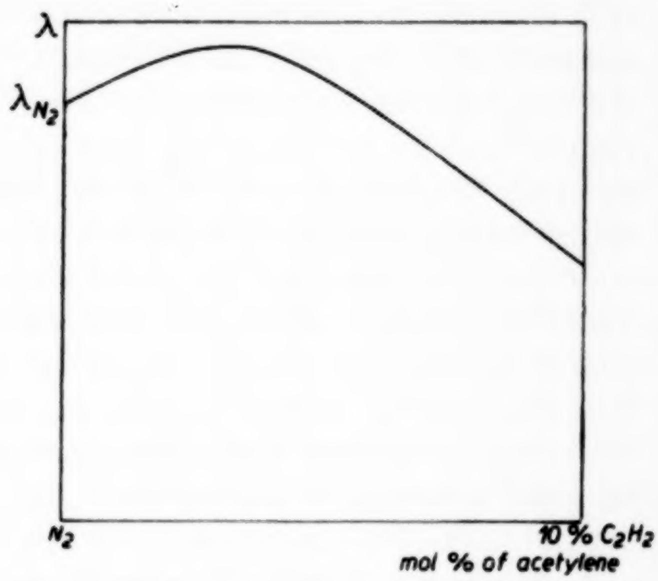

Fig. 2. Thermal conductivity of nitrogen-acetylene mixtures (schematic).

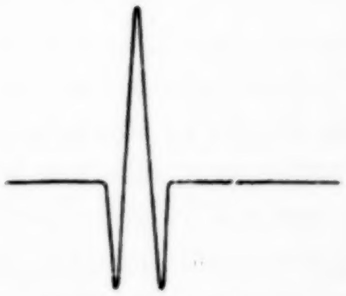

Fig. 3. Elution peak of C_2H_2 in N_2.

In the following sections, dealing with the calibration of a thermal conductivity detector, it will be assumed that the response of the instrument is directly proportional to $\triangle\lambda$. This condition is fulfilled fairly closely in a katharometer of proper design.

CALIBRATION BY PEAK HEIGHT OR PEAK AREA?

In G.L.C. a sample of the mixture to be analysed is introduced into as narrow a band of the column as possible. The record of the components emerging consists of a series of peaks having certain widths. In favourable circumstances the elution curve, which represents a plot of detector response against time, bears almost symmetric Gaussian peaks. If the response is a linear function of the concentration of a component in the column effluent and if the volumetric gas rate at the column outlet is constant, the area of a peak is a direct measure of the amount of a component. Calibration then simply consists in measuring the response for a given concentration of the component under the same conditions as those prevailing in the actual analysis. As the response is dependent on a number of operational variables, it is essential to minimize fluctuations in these variables. It has been found, for instance, that the instrument must be thermostatted and the voltage supplied to the heating filaments must be closely stabilized. Slight fluctuations in column temperature do not affect the peak area, fluctuations in flow, however, impair the accuracy because the area is an integral over time (at a constant speed of the recorder chart), whereas the amount of a component requires integration over the volume of the emerging gas. Generally the gas flow can easily be kept constant to a sufficient degree; during the appearance of a band, however, the amount of component leaving the column as vapour is added to the stream of carrier gas. The resulting increase in flow is proportional to the concentration of the component in the column effluent. This effect cannot easily be calculated. It is, of course, small for small amounts of a component; for large quantities the calibration factors will depend upon the amount of component, irrespective of the type of detector.

A drawback of employing peak areas for quantitative interpretation is that their measurement is more troublesome. In this respect the height of the peak is a more convenient parameter. Peak heights, however, are in general much more sensitive to changes in the variables operative in G.L.C. than peak areas. An important consideration is that even in a completely linear system the peak height cannot be strictly proportional to the amount of component, except for very small samples where the width of the peak is not yet affected by the sample size.

Whilst the peak area has been seen to be sensitive to fluctuations in flow, this is virtually not the case for peak heights; the latter, however, are very sensitive to fluctuations in column temperature.

Generally speaking, therefore, peak area is the more reliable parameter for calibration, but peak height is easier to use. Both find their applications, depending on the requirements of a particular case. The advantages of the peak height for routine purposes are very definite (particularly with a view to automatization) and it is therefore worth while considering the conditions under which this parameter may successfully be employed. An attempt in this sense has been made by DIMBAT, PORTER AND STROSS and others[9]. These authors showed that if the sample is not introduced into the column as a plug, but is swept with "perfect mixing" by the carrier gas from a sample chamber, the peak width is almost independent of the amount of component; the peak height will therefore then be proportional to this amount.

Only some of the reasons for which calibration is necessary have been discussed above. Owing to the diversity of factors, conditions vary from case to case, and on this account several different forms of calibration have been developed. An important procedure that can be mentioned in passing is the calibration technique employing an "internal standard", as developed by RAY[10], in which a known quantity of a compound (a "marker") is added to the sample. In the present paper we shall confine ourselves to a practical example showing the procedures that can be followed for obtaining an accurate quantitative analysis directly from calibrations performed on mixtures of the pure components present in the sample.

QUANTITATIVE ANALYSIS OF NARROW INDUSTRIAL HYDROCARBON FRACTIONS

The example to be quoted deals with cuts obtained in the "super-fractionation" of hexane, an efficient technical distillation method for effecting a separation of the branched-chain hexanes from *n*-pentane and *n*-hexane, closely adjacent to the former in boiling point. The efficiency of this separation can be controlled by spectroscopic or spectrometric methods, but G.L.C. has proved to be very convenient and reliable for the purpose.

The analysis of three fractions will be considered: the first fraction contains the bulk of the *n*-pentane, the second fraction the main amount of the *iso*hexanes, the third the greater part of the *n*-hexane.

The components to be estimated are enumerated with their boiling points in Table I.

TABLE I

COMPONENTS TO BE ESTIMATED IN HEXANE DISTILLATION FRACTIONS

	Component	*B.pt. °C*
	n-pentane (*n*-C_5)	36.0
	cyclopentane (c.p.)	49.2
	2.2-dimethylbutane (neo-C_6)	49.7
"*iso*hexanes"	2.3-dimethylbutane (2.3-dmb)*	58.0
	2-methylpentane (2-m C_5)*	60.3
	3-methylpentane (3-m C_5)	63.2
	n-hexane (n-C_6)	68.8

* Under the conditions employed for G.L.C. analysis, using dimethylsulfolane as stationary phase, 2.3-dmb could not be separated from 2-m C_5. These components have hence been pooled for the analysis, and in the subsequent calibration only 2-m C_5 is employed.

Since it is necessary to know, for purposes of calibration, what ranges of composition must be considered, these ranges were predicted by calculation from the characteristics of the distillation system and the base materials employed. They were:

n-*pentane fraction*	iso*hexane fraction*	n-*hexane fraction*
70 - 100% *n*-C_5	80 - 100% *iso*-C_6	70 - 100% *n*-C_6
20 - 0% c.p.	15 - 0% c.p.	30 - 0% c.p. + *iso*-C_6
10 - 0% *iso*-C_6	5 - 0% *n*-C_5	
	2 - 0% *n*-C_6	

For the analyses by G.L.C. and the calibrations to be described here, equipment of conventional design was employed. The conditions** maintained in the separations are listed in Table II.

CALIBRATION OF THE THERMAL CONDUCTIVITY DETECTOR FOR THE CASE IN VIEW

In the procedures of calibration to be described below, the areas of the peaks have been used as basis.

If a mixture containing percentages by weight A, B, *etc.* of various components

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** As is frequently the case in industrial analyses by G.L.C., the conditions maintained were not the best that could be devised. This was due to considerations of a practical nature (available facilities, safety, skill of personnel, etc.)

TABLE II

EXPERIMENTAL CONDITIONS MAINTAINED

Column	: 720 × 0.6 cm internal diameter, coiled copper tubing.
Column temperature	: 30° ± 0.1°C.
Stationary liquid	: dimethylsulfolane.
Support	: ground firebrick (Sterchamol No. 22), 30/50 mesh.
Ratio solvent : support	: 40 : 100 (wt/wt).
Carrier gas	: nitrogen.
Column pressure	: inlet, 20 mm Hg above atm; △p = 400 mm.
Gas rate	: 90 ± 0.5 ml/min at outlet pressure.
Sample introduction	: by syringe.
Sample size	: approx. 50 µl.
Katharometer bridge current	: 100 ± 0.5 mA.

yields elution peaks having areas equal to I_A, I_B, *etc.* respectively, the calibration factors f_A, f_B, *etc.* are those factors by which the corresponding areas must be multiplied in order that the products may be proportional to A, B, *etc.*; the latter percentages may then be determined by proportioning the products over their sum:

$$\frac{A}{100} = \frac{f_A I_A}{f_A I_A + f_B I_B + \ldots} \quad \ldots\ldots\ldots\ldots \quad (1)$$

Since we have a set of homogeneous equations,totalling(1), for all of the components, we can arbitrarily assign a calibration factor of unity to one component (the "internal marker") present say in a percentage R. For any other component (quantity present: C per cent by weight) we then have the relationship

$$f_C = \frac{C.I_R}{R.I_C} \quad \ldots\ldots\ldots\ldots \quad (2)$$

For the purpose of calibration in the present case, mixtures in various proportions were made of the pure components present in the three fractions investigated, within the range studied. These synthetic mixtures are listed as 1, 2, 3, *etc.* in Table III, and their true compositions (*viz.* the amounts blended) are indicated in the rows *a* against each component.

These blends were submitted to separation by G.L.C. under the afore-mentioned conditions. For the purpose of illustration one elution diagram for each group of blends is reproduced here in Figs. 4a, b and c. It will be seen that in the case of Fig. 4c (corresponding to a blend used in calibrating for the *n*-hexane fraction) the peak for cyclopentane is largely masked, and that for 3-methylpentane partially masked by the main *n*-hexane peak. (The minimum between cyclopentane and n-C_6 actually disappears at lower percentages of c.p.) In the analysis of this fraction the latter two components were therefore pooled.

The areas of the peaks were determined automatically by means of an integrating device: a low-inertia d.c. electromotor, fed from the recording network, and provided with a counter.

The "internal markers" chosen for the three groups of blends were cyclopentane (for the *n*-pentane and "*iso*hexane" groups) and *n*-hexane for the *n*-hexane group. f_C was calculated in each case by formula (2) from the area I of the peaks. As an example, the areas from three runs are given in Table IV for blend 6 (Table III B), together with the calculated values of f_C.

The values of the calibration factors so determined for the various blends are shown in the rows marked f_C in Tables III A, B and C.

A comparison of rows *a* and f_C in the tables makes it evident that the calibration factors vary (though not to a very pronounced extent) with the amount in which the component is present. In view of this fact the question arises how these factors are to be employed in analysing an unknown blend, which may be expected to have an intermediate composition within the range investigated.

TABLE III

CALIBRATION DATA

a = true percentage (wt)
b = percentage of *I* (uncorrected)
c = percentage calculated with fc
d = percentage calculated with graphical factor
$\bar{f}c$ = average of fc

A. Data relative to calibration with synthetic blends for n-*pentane fraction*

Blend		*1*	*2*	*3*	*4*
n-pentane	*a*	68.62	79.39	87.49	95.15
	b	62.5	73.7	82.7	93.1
	c	69.3	79.5	86.9	95.2
	d	68.8	79.3	87.6	—
	fc	1.42	1.46	1.52	1.46
			$\bar{f}c$ = 1.46		
2-methylpentane	*a*	10.61	5.12	2.77	—
	b	10.7	5.4	3.3	—
	c	10.3	5.0	3.0	—
	d	10.6	5.1	2.9	—
	fc	1.28	1.28	1.22	—
			$\bar{f}c$ = 1.26		
cyclopentane	*a*	20.77	15.49	9.74	4.85
	b	26.8	20.9	14.0	6.9
	c	20.4	15.5	10.1	4.8
	d	20.8	15.6	9.5	—
	fc	1.00	1.00	1.00	1.00

B. Data relative to calibration with synthetic blends for "isohexane" *fraction*

Blend		*5*	*6*	*7*	*8*	*9*
n-pentane	*a*	1.62	3.24	6.31	8.59	11.38
	b	1.8	3.2	6.3	8.5	11.3
	c	1.7	3.3	6.3	8.5	11.2
	d	1.8	3.2	6.3	8.5	11.2
	fc	1.23	1.31	1.33	1.33	1.34
				$\bar{f}c$ = 1.31		
2.2-dimethylbutane	*a*	2.23	4.33	8.73	3.29	2.32
	b	2.3	4.1	8.2	3.1	2.3
	c	2.3	4.4	8.6	3.2	2.3
	d	2.4	4.3	8.7	3.2	2.4
	fc	1.32	1.38	1.40	1.40	1.40
				$\bar{f}c$ = 1.38		
2-methylpentane	*a*	71.89	46.86	52.21	59.27	63.41
	b	67.3	43.6	49.1	55.7	59.8
	c	71.2	47.7	52.6	59.4	63.3
	d	71.4	46.6	52.4	59.1	63.6
	fc	1.44	1.38	1.40	1.40	1.40
				$\bar{f}c$ = 1.40		

TABLE III (continued)

Blend		5	6	7	8	9
3-methylpentane	*a*	10.55	21.83	14.30	15.91	10.99
	b	11.0	21.1	14.2	16.0	11.3
	c	10.9	21.4	14.2	16.0	11.2
	d	10.7	22.0	14.3	16.3	11.1
	f_C	1.29	1.31	1.31	1.31	1.28
				f_C = 1.30		
n-hexane	*a*	3.67	10.94	7.83	1.20	2.21
	b	4.1	11.5	8.4	1.3	2.5
	c	3.7	10.7	7.7	1.2	2.3
	d	3.7	10.0	7.9	1.1	2.2
	f_C	1.19	1.21	1.19	1.19	1.18
				f_C = 1.19		
cyclopentane	*a*	10.04	12.80	10.62	11.74	9.69
	b	13.5	16.5	13.8	15.4	12.8
	c	10.2	12.8	10.6	11.7	9.7
	d	10.0	12.9	10.4	11.8	9.5
	f_C	1.00	1.00	1.00	1.00	1.00

C. Data relative to calibration with synthetic blends for n*-hexane fraction*

Blend		10	11	12	13
2-methylpentane	*a*	8.40	5.64	1.97	1.68
	b	8.3	5.7	2.1	1.8
	c	8.1	5.5	2.0	1.7
	d	8.5	5.8	2.0	1.7
	f_C	1.03	1.00	0.92	0.92
			f_C = 0.97		
3-methylpentane	*a*	15.89	12.96	7.70	3.45
	b	15.4	13.2	8.1	3.9
	c	14.9	12.8	7.8	3.8
	d	15.6	13.3	7.7	3.2
	f_C	1.04	0.98	0.95	0.88
			f_C = 0.96		
n-hexane	*a*	75.71	81.40	90.33	94.87
	b	76.3	81.1	89.8	94.3
	c	77.0	81.7	90.2	94.5
	d	75.9	81.4	90.3	94.9
	f_C	1.00	1.00	1.00	1.00

Two procedures have been considered here.

(a) An average value of f_C is employed for all analyses within the range. (This average is given as f_C in Tables III). The compositions calculated with these average factors are given in the rows *c* in the tables. This procedure, which is obviously the most convenient, might be expected to be somewhat less precise than the following one.

(b) A graphical interpolation method may be used, taking into account the composition of the actual blend investigated. This was done by plotting the percentage area for each component (*viz.* 100 I_C/I_{total}) against the percentage (weight) of component in the blend. The plot for 3-methylpentane, so obtained, is shown in Fig. 5, which includes points for both the "*iso*hexane" and

References p. 39.

TABLE IV

PEAK AREAS AND VALUES OF f_C FOR BLEND 6

Component	I_C *(arbitrary units)*			*Per cent of comp. (wt)*	f_C *(mean)*
n-pentane	165	162	170	1.62	1.23
2.2-dimethylbutane	212	210	217	2.23	1.32
2-methylpentane	6294	6372	6279	71.89	1.44
3-methylpentane	1016	1040	1031	10.55	1.29
n-hexane	380	396	390	3.67	1.19
cyclopentane (marker)	1250	1285	1263	10.04	(1.00)
Total area*	9317	9465	9350		

* The total area is of interest, since it shows that introduction by syringe gives reasonably reproducible quantities.

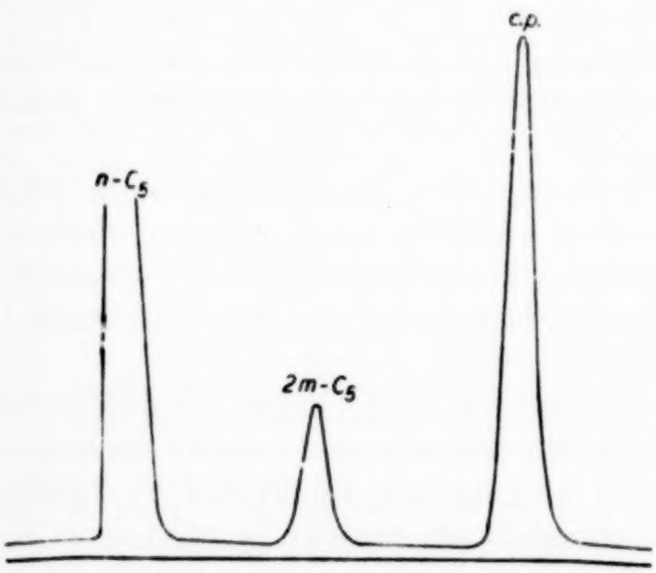

Fig. 4a. Elution curve of blend of components in *n*-pentane fraction.

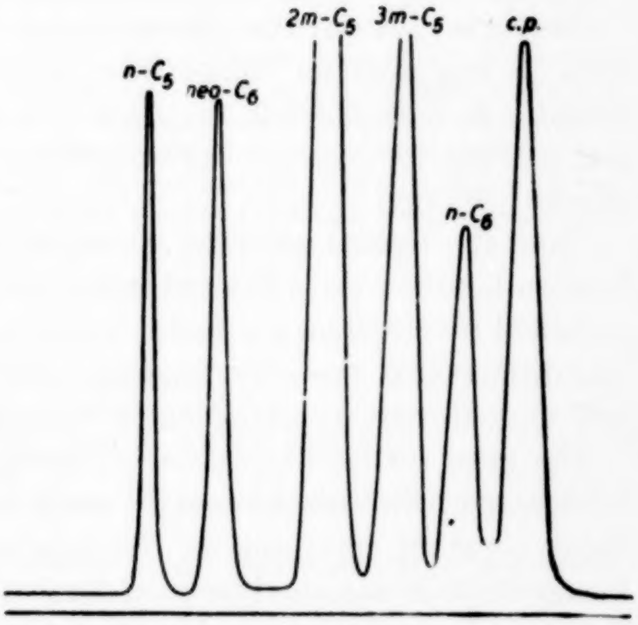

Fig. 4b. Elution curve of blend of components in *iso*hexane fraction.

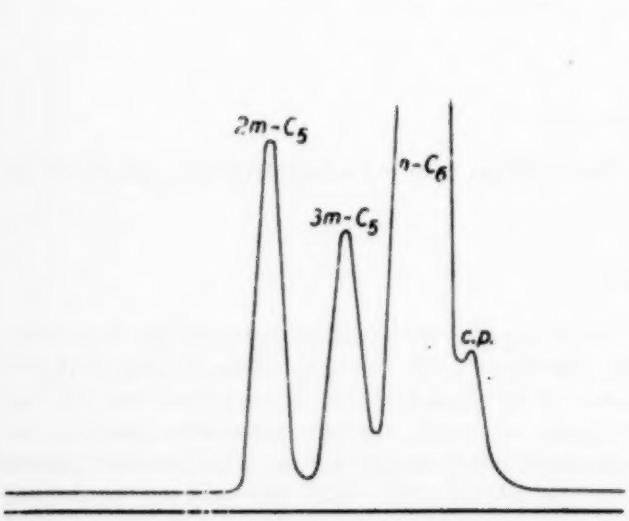

Fig. 4c. Elution curve of blend of components in *n*-hexane fraction.

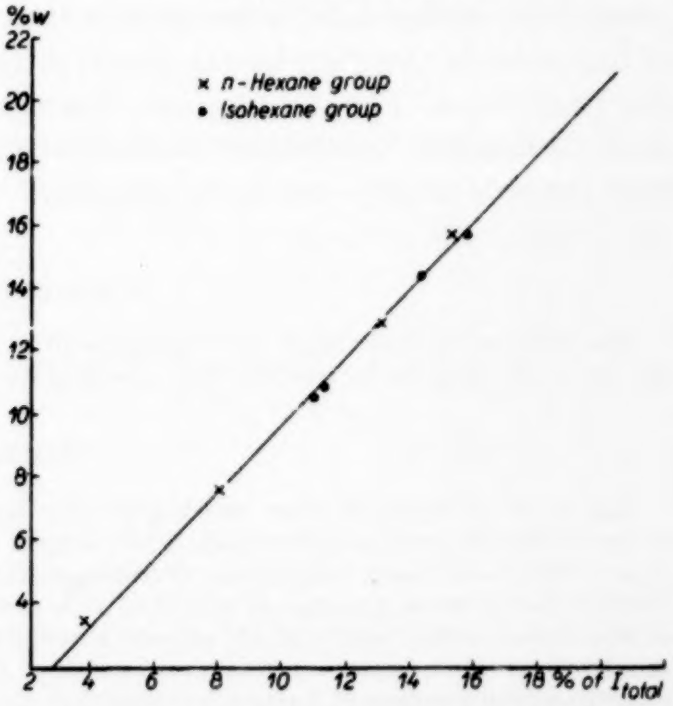

Fig. 5. Percentage of total peak area against percentage by weight for 3-methylpentane.

the "*n*-hexane" group of calibrations. (As a rule a separate graph will have to be made for each group of mixtures.) It was found that over the range studied the plot could be represented by a straight line not passing through the origin on extrapolating. Such a graph, or the linear equation derived from it, can be used directly for converting "percentage of I" into "percentage by weight of component". These values are given in Tables III in the rows marked *d*. In the case of 3-methylpentane, which is present in each of the three hydrocarbon fractions, the linear expressions read respectively:

n-pentane fraction : $C = 105\ I_C/I_{total} - 0.6$
"*iso*hexane" fraction : $C = 108\ I_C/I_{total} - 1.1$
n-hexane fraction : $C = 105\ I_C/I_{total} - 0.2$

(C stands, as before, for the percentage by weight).

Tables III A, B and C also give — in the rows marked *b* — the percentage $100\ I_C/I_{total}$, which corresponds to the amount of component that would be found by the area method if all the calibration factors were unity.

CONCLUSIONS

The data given in the present paper mainly serve to show (a) that on the whole (and in any case for major components) calibration of the thermal conductivity detector is indispensible in G.L.C. for determining the quantities of components, and (b) that by a proper determination of calibration factors very satisfactory data can be obtained.

From the figures given in the tables it can be seen that the use of average calibration factors over a limited range perhaps gives a slightly lower accuracy than is obtained by employing a factor which is variable with composition (rows *c* versus *d*). The difference is, however, not large, and the former method (which is less troublesome) will undoubtedly be satisfactory in most cases.

The need for calibration is undoubtedly a drawback, particularly for incidental analyses; in the case of routine work involving the analysis of a product having a fairly constant composition, the time required is of far less importance. It should be noted that the conditions of analysis described in the present paper are in so far not ideal, that the calibration factors are relatively large. By modifying the conditions (and especially by using hydrogen or helium instead of nitrogen) it is possible to realize calibration factors that are far closer to unity. The percentages of components can then be calculated directly, with much lower discrepancies, from the peak areas. The authors are, however, of the opinion that even under these more favourable conditions calibration cannot be entirely dispensed with if the best possible results are to be obtained.

ACKNOWLEDGEMENT

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SUMMARY

The form of detector now most generally used in gas-liquid chromatography is the katharometer (thermal conductivity cell). This detector, in common with certain other "differential" types that have been employed, requires calibration for a quantitative interpretation of the elution curve, since the signal recorded is not dependent on some simple molecular parameter of the eluted component and also is not a linear function of its concentration. The present paper mentions several causes of this non-linearity. It further illustrates, with the aid of practical examples (the analysis of narrow hydrocarbon distillates) how the katharometer can be calibrated by analysing mixtures of the pure components in question, and how the calibration factors are applied in the quantitative interpretation of analyses.

RÉSUMÉ

Le modèle de détecteur le plus généralement utilisé actuellement pour la chromatographie de partage entre liquide et gaz est le katharomètre (cellule de conductibilité thermique). Cet appareil de détection, comme certains autres types d'appareils "différentiels" employés, nécessite un étalonnage pour une interprétation quantitative de la courbe d'élution, le point enregistré n'étant pas dépendant d'un paramètre moléculaire simple du constituant élué et n'étant pas non plus une fonction linéaire de sa concentration. Les auteurs donnent plusieurs causes de cette non-linéarité. Ils illustrent ensuite, par des exemples pratiques (analyse de fractions d'hydrocarbures obtenues par un fractionnement très poussé) comment le katharomètre peut être calibré par des analyses de mélanges des constituants purs en question et comment les facteurs d'étalonnage sont appliqués à l'interprétation quantitative des analyses.

ZUSAMMENFASSUNG

Der Detektionsapparat, welcher gegenwärtig am meisten in der Gas-Flüssigkeitschromatographie verwendet wird, ist das Katharometer (Wärmeleitfähigkeitszelle). Dieser Detektor erfordert, ebenso wie gewisse andere „Differential"-Typen, eine Kalibrierung zur quantitativen Interpretation der Elutionskurve, da das aufgezeichnete Signal nicht von einem einfachen molekularen Parameter des eluierten Bestandteils abhängt und auch keine einfache Funktion dessen Konzentration ist. In der vorliegenden Arbeit werden mehrere Gründe für diese nichtlineare Abhängigkeit angeführt. Weiters wird, mit Hilfe praktischer Beispiele (Analyse von stark fraktionierten Kohlenwasserstoffdistillaten) gezeigt, wie das Katharometer durch Analyse von Gemischen der betreffenden reinen Komponenten geeicht werden kann und wie die Eichungsfaktoren bei der quantitativen Interpretation der Analysen angewendet werden.

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A STUDY OF CHROMIUM(III) SULPHATE COMPLEXES BY ELECTROPHORESIS ON FILTER PAPER

by

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The formation of complexes between sulphate ions and chromium(III) ions has been the subject of numerous investigations[1] as chromium sulphate has important uses in industry[2]. It was suggested to us by Dr. M. HAISSINSKY to develop an analytical method for the separation of Cr(III) and Cr(VI) to be used in studies of the radiochemistry of the Cr(III)/Cr(VI) equilibrium. We had already observed the electromigration both of Cr(III) complexes and CrO_4^{-2} ions (see ref.[7]) and hence a paper electrophoresis method was worked out. This method and its results in radiochemistry were described separately with M. LEFORT[3].

Paper electrophoretic studies of chromium-oxalato and chromium-sulphato complexes had been published by SHUTTLEWORTH[4] and KAWAMURA *et al.*[5,6]. All these were concerned with problems encountered in tanning chemistry. Using dilute acids as electrolyte they tried to establish the charge on the various complexes formed.

Instead of examining conditions encountered in tanning we used a simpler system, that of an aqueous solution of $KCr(SO_4)_2 \cdot 12\,H_2O$ as we were interested in the possibility of the formation of complexes which would migrate with the same speed as chromate ions and thus interfere in the separation Cr(III)-Cr(VI). We also carried the investigation one step further than SHUTTLEWORTH[4] and KAWAMURA[5,6] by marking the sulphate present with radioactive ^{35}S added as carrier-free tracer $H_2{}^{35}SO_4$.

The radioactivity ratio between the sulphate band and that of the various coloured Cr(III) complexes was measured and thus a quantitative estimate of the amount of sulphate complexed under various conditions could be obtained. In cold solutions SO_4^{-2} ions are taken up only very slowly by the Cr(III) ions as shown in the experimental part below. At elevated temperatures there is a rapid uptake of sulphate ions.

EXPERIMENTAL

A simple apparatus was used[7], consisting of two glass plates holding the paper strip, which has its ends dipping into beakers containing the electrolyte and inert electrodes.

Paper strips 3 × 36 cm (Papeterie d'Arches No. 302) were wetted with the electrolyte and placed on a filter paper in order to drain off excess liquid. The chromium solution to be analysed was then applied from a micropipette along the starting line which was at the centre of the band, leaving a margin of 2 mm on each side.

As electrolyte a solution of sodium sulphate (5%) containing a little free H_2SO_4 (*N*/10) was chosen so as to reduce the possibility of dissociation by maintaining approximately the same sulphate concentration as during formation of the complexes and also to prevent undue hydrolysis by the presence of H^+ ions. The sharpness of the separated bands seems to indicate that this was achieved. As starting solution in all cases a 15% w/v solution of chrome alum was taken. A potential of 150 volt for 40 minutes was applied throughout. Radioactivity measurements were carried out using a mica end window counter for soft beta rays. The paper bands were placed on a lead plate (4 mm thick) with a 5 mm or a 2 mm window. According to WINTERINGHAM *et al.*[8] the error due to self absorption in the paper is 6.5% for a variation of paper thickness of 10%.

RESULTS

a. Ageing of solutions at room temperature

In this investigation all experiments were carried out with the same solution, which was stored in a glass-stoppered tube at room temperature. The results are shown in Fig. 1. The cationic bands of blue or purple colour were noted to be free sulphate. Green bands make their appearance after 24 hours and always correspond

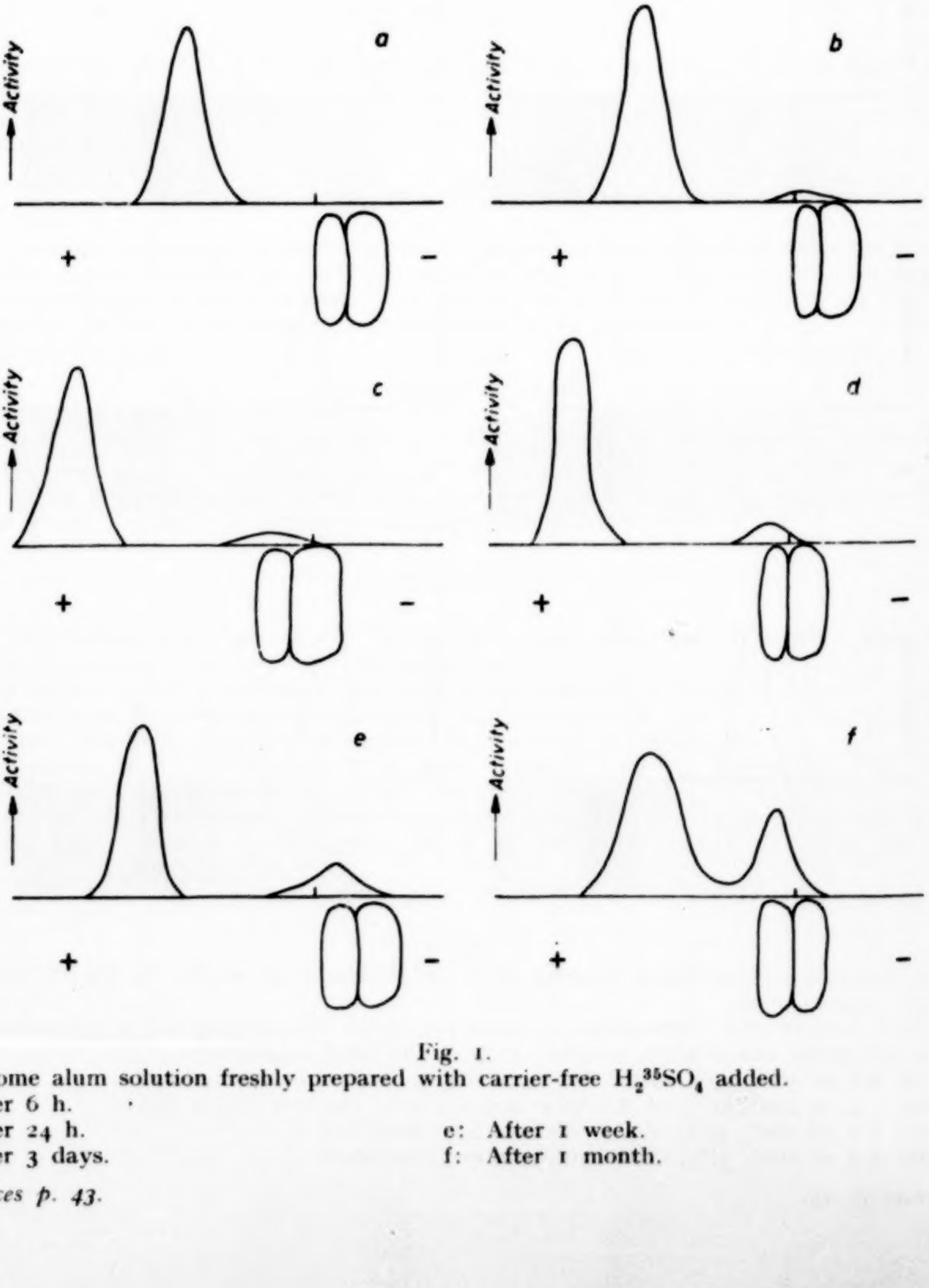

Fig. 1.

a: Chrome alum solution freshly prepared with carrier-free $H_2{}^{35}SO_4$ added.
b: After 6 h.
c: After 24 h.
d: After 3 days.
e: After 1 week.
f: After 1 month.

to a radioactive peak. However the uptake of sulphate is rather slow and after one week only 15% of the total sulphate entered into combination with the Cr(III) ions.

b. Heating a solution

A freshly prepared chrome alum solution was boiled in a tube over a naked flame. An immediate colour change from blue-violet to green took place. The solution was brought twice to boiling and was analysed immediatly. Three well distinguished bands could be separated: a blue cationic one, a green one and a deep green one both moving anionically. 43% of the total sulphate was found in the two green bands.

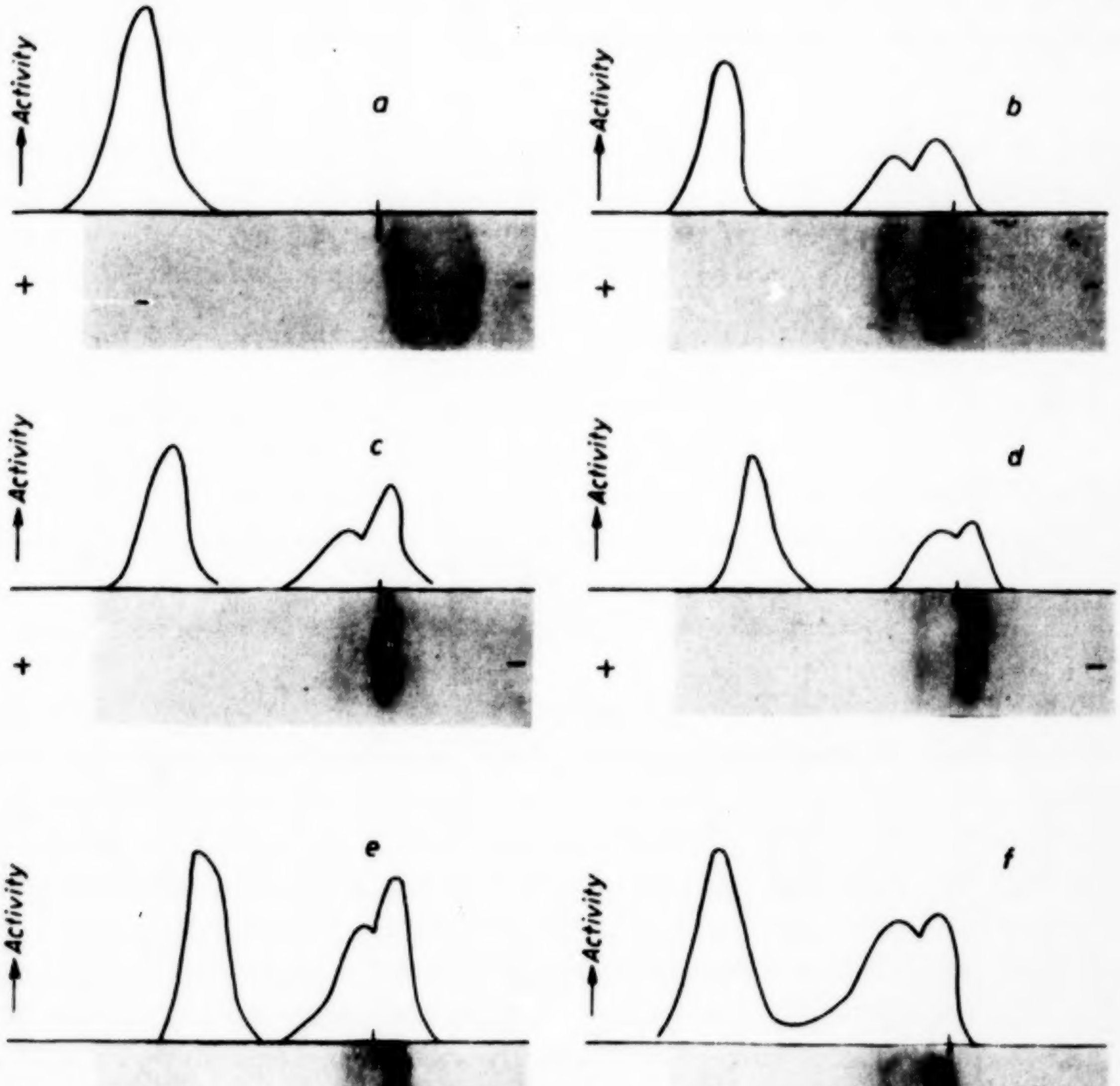

Fig. 2.

a: Chrome alum solution before heating. Both Cr(III) bands are purple. All the ^{35}S moves as a single anionic band.
b: After 1 hour at 100°. Three coloured bands are visible. Two correspond to radioactive peaks and are green and contain together 45% of the total sulphate.
c: After 2 h at 100°. 49% of the total activity is in the two visible bands.
d: After 4 h at 100°. 50% of the total activity is in the two visible bands.
e: After 6 h at 100°. 53% of the sulphate are complexed.
f: After 8 h at 100°. 58% of the sulphate are complexed.

References p. 43.

c. Heating at 100°C for prolonged periods

The freshly prepared chrome alum solution was heated on a water bath in a well stoppered flask and samples withdrawn at various times. The results are shown in Fig. 2. As the electro-osmotic flow is somewhat variable, neutral or almost neutral complexes may sometimes travel slightly to the cathode and sometimes slightly to the anode. It appears that the complexing reaction is rather fast and most of the sulphate enters the Cr(III) complexes immediately. In this series of experiments as in the above all green complexes contained sulphate while blue or purple bands were free of SO_4^{-2} groups.

ACKNOWLEDGEMENT

One of us (S.K.) acknowledges a French Government Scholarship and the aid granted by the American Friends of the Hebrew University.

SUMMARY

Paper electrophoresis in combination with radioactive tracer techniques permits the investigation of the reactions of Cr^{+3} with SO_4^{-2}. According to our results green solutions contain invariably complexed SO_4^{-2} groups. The kinetics of the uptake of SO_4^{-2} was also studied at two different temperatures.

RÉSUMÉ

L'électrophorèse sur papier, combiné à des techniques radiochimiques utilisant les traceurs radioactifs a permis d'étudier les réactions entre les ions Cr^{+3} et SO_4^{-2}. D'après les résultats obtenus, les solutions vertes renferment toujours des groupes SO_4^{-2} complexés. La cinétique de l'absorption de SO_4^{-2} a été étudiée à deux températures différentes.

ZUSAMMENFASSUNG

Mit Hilfe der Papierelektrophorese und von radioaktiven „tracer"-Verfahren konnten die Reaktionen zwischen Cr^{+3} und SO_4^{-2} untersucht werden. Auf Grund der erhaltenen Ergebnisse enthalten grüne Lösungen immer komplex gebundene SO_4^{-2}-Gruppen. Die Kinetik der SO_4^{-2}-Aufnahme wurde ebenfalls bei zwei verschiedenen Temperaturen studiert.

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DOSAGE COLORIMÉTRIQUE DE L'URANIUM PAR LE DIBENZOYLMÉTHANE

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Les travaux de J. H. Yoe, F. Will et R. A. Black[1] ont montré que le dibenzoylméthane (dbm) constituait un excellent réactif colorimétrique de l'uranium. Ces auteurs en ont déterminé les conditions d'emploi et ont étudié le comportement de quelques ions autres que l'uranium dans les conditions de pH et de milieu utilisées.

J. A. S. Adams et William S. Maeck[2] ont repris l'étude du réactif. Ils recommandent l'extraction du nitrate d'uranyle par l'acétate d'éthyle et le développement de la coloration en présence du solvant à un pH apparent de 4 que l'on doit ensuite porter à 7 avant la mesure.

Nous avons entrepris la recherche de conditions opératoires aussi simples que possible, permettant la détermination de l'uranium dans les conditions les plus générales, en évitant tout ajustage de pH et toute extraction par solvant.

I. MILIEU UTILISÉ POUR LE DÉVELOPPEMENT DE LA COLORATION

Le milieu utilisé devait remplir les conditions suivantes:

1° Dissoudre le dibenzoylméthane,
2° Posséder une très forte capacité tampon à un pH apparent de l'ordre de 6 à 7,
3° Ne pas provoquer la précipitation d'hydroxydes,
4° Ne pas former avec l'uranium un complexe empêchant l'action du dbm.

Les deux premières conditions ont été remplies par l'emploi d'un mélange d'eau et de pyridine en parties égales; les deux autres par l'addition d'acide éthylènediaminotétracétique.

En ce qui concerne la concentration du dibenzoylméthane, nous avons constaté qu'une quarantaine de mg dans 25 ml correspondaient pratiquement au maximum asymptotique de la densité optique dans notre milieu hydropyridinique (Fig. 1).

Nous avons donc, dans la suite des essais, utilisé la solution suivante:

Sol. C	Dibenzoylméthane pur	2	g
	Ac. éthylènediaminotétracétique pur	12.5	g
	Pyridine pure incolore	500	ml
	Eau qsp	1000	ml

Bibliographie p. 56.

Cette solution s'emploie à raison de 20 ml environ pour 5 ml de solution aqueuse acide d'uranium. La Fig. 2 montre la forme des courbes $D = f(\lambda)$ pour la solution colorimétrique relativement à un essai à blanc.

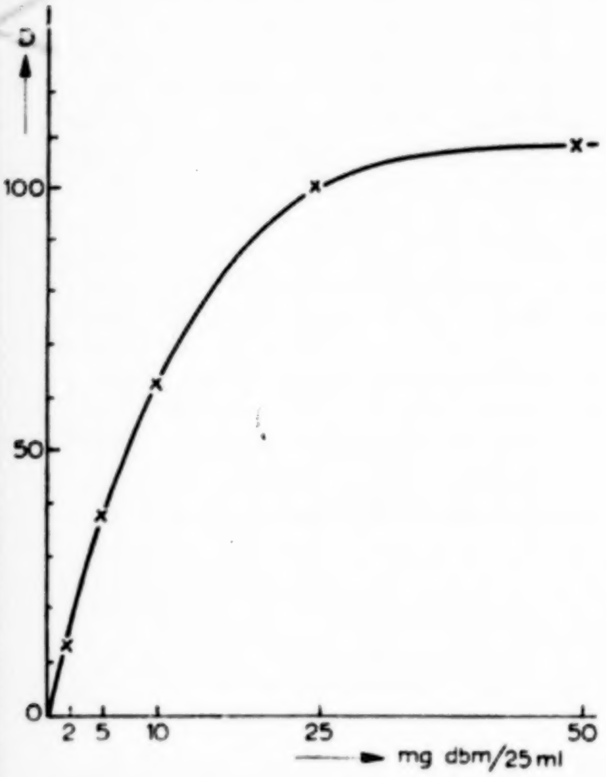

Fig. 1. Influence de la quantité de dibenzoylméthane

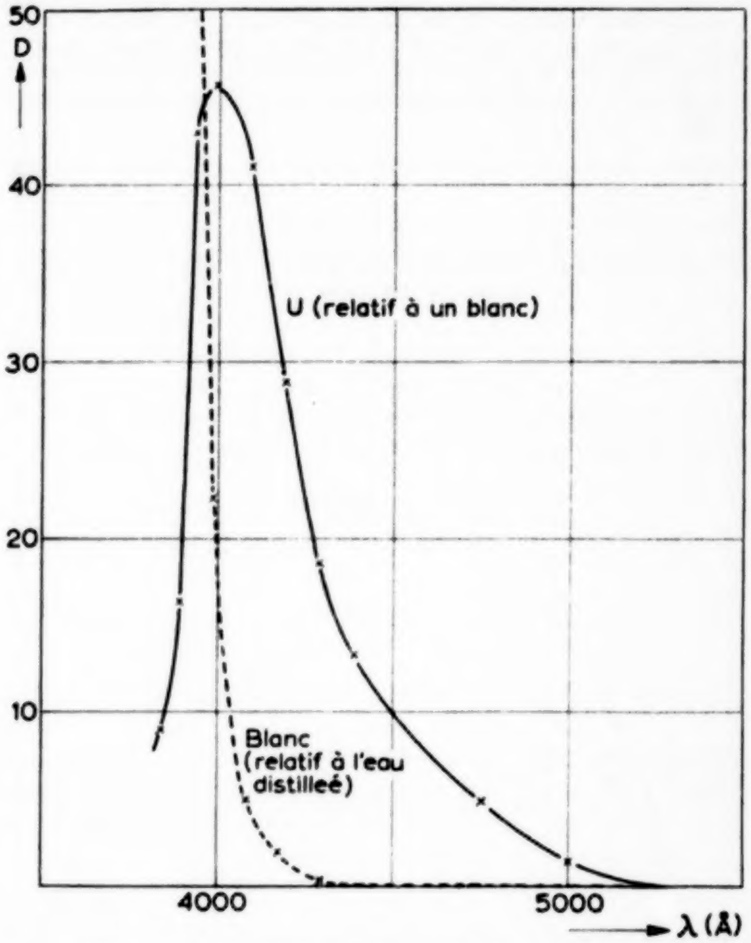

Fig. 2. Absorption de l'essai à blanc et du complexe uranique

Le maximum d'absorption est situé à 400 mμ. Toutefois, des raisons relatives à l'élimination des interférences conduisent à sacrifier légèrement la sensibilité et à effectuer les mesures à 415 mμ. On a alors en outre l'avantage d'un essai à blanc faible.

2. FORMULE DU COMPLEXE U + dbm

Nous avons déterminé le rapport moléculaire U/dbm dans nos conditions opératoires, (c'est-à-dire pour un milieu correspondant à la solution C où l'on a fait varier la concentration en dbm et l'addition d'uranium), suivant la méthode des variations continues de JOB. La Fig. 3 montre que l'on a U/dbm = 1/1.

Dans un milieu hydroalcoolique de pH apparent voisin de 7, J. H. YOE, F. WILL ET R. A. BLACK[1] avaient obtenu U/dbm = 2/1.

Si on se reporte à la courbe $D = f(\text{pH})$ (Fig. 4) tracée par J. A. S. ADAMS ET WILLIAM S. MAECK[2], on constate que les points expérimentaux sont compatibles avec l'existence d'un palier et d'un maximum, susceptibles de correspondre à deux complexes différents.

3. SOLUTIONS ET APPAREILS UTILISÉS

— Acide tartrique à 500 g/l
— Alcool éthylique à 5%
— Solution à 150 g/l de Na_2CO_3 anhydre dans l'eau distillée

Bibliographie p. 56.

— Les mesures ont été effectuées au moyen des spectrophotomètres ,,Jean et Constant'' pour les études d'interférence, et ,,Jobin et Yvon'' pour les courbes $D = f(\lambda)$.

Solution étalon d'uranium E_1

Attaquer 250.0 mg de U_3O_8 pur par 10 ml de $HClO_4$. Transvaser quantitativement dans une fiole jaugée de 1 litre et compléter au volume avec de l'eau distillée (1 ml → 0.25 mg U_3O_8).

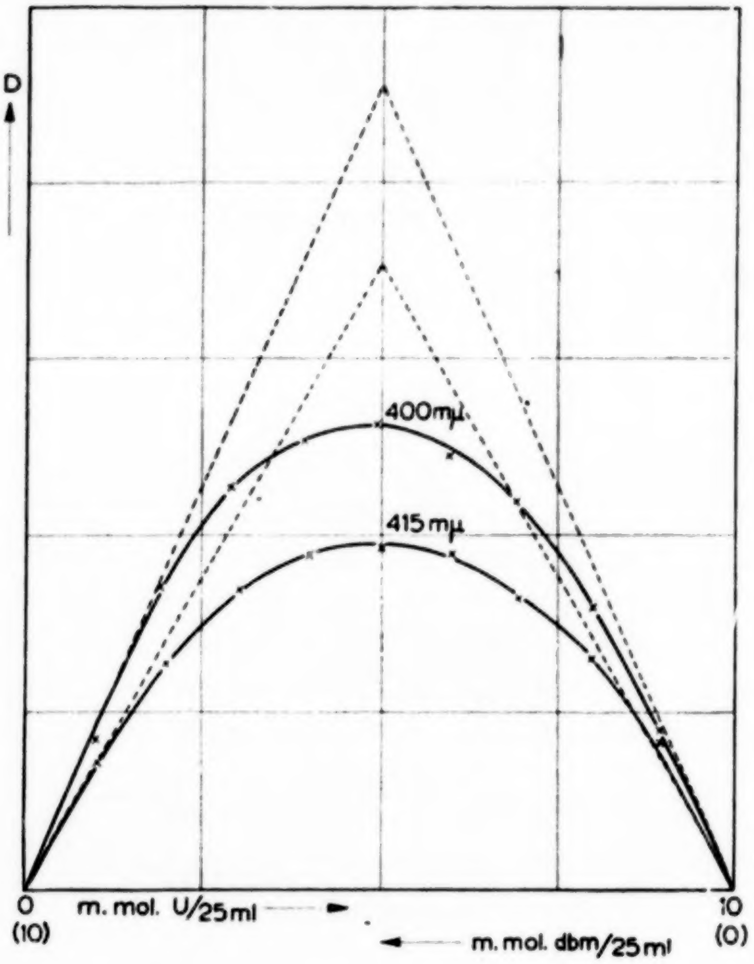

Fig. 3. Méthode des variations continues de Job

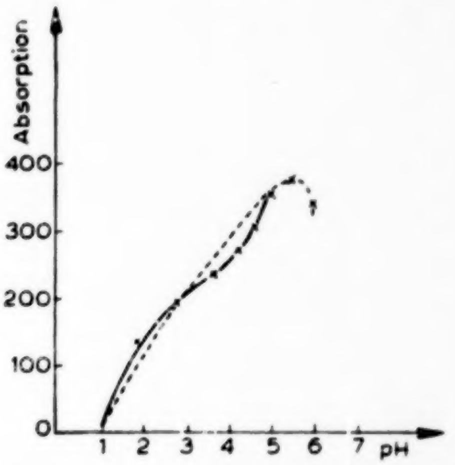

Fig. 4. Densité optique en fonction du pH (d'après J. A. S. Adams et William S. Maeck[2])

Solution étalon d'uranium E_2

Attaquer de même 1.25 g de U_3O_8 pur par 10 ml de $HClO_4$ et porter à 500 ml avec H_2O (1 ml → 2.5 mg U_3O_8).

Liqueur ferrique F

$FeCl_3$ (solution commerciale à 45° Bé)	300 ml
H_3PO_4 à 85% (voir paragr. 4, note e)	15 ml
$HClO_4$ commercial	500 ml
Eau distillée qsp.	2000 ml

Solution colorimétrique C

(Voir paragraphe 1)

4. MODE OPÉRATOIRE

a) *($U_3O_8 < 0.50\%$)*

1) Introduire 250 mg ± 0.2 de minerai, passant au tamis Afnor no. 18 (50 microns), dans un bécher Pyrex de 50 ml.*

2) Ajouter 1 ml H_2SO_4 concentré. Porter sur bain de sable très chaud jusqu'à cessation du dégagement de fumées blanches. Terminer l'évaporation à sec en chauffant le bécher tenu à la pince dans la flamme d'un bec Meker afin de volatiliser l'acide sulfurique condensé sur les parois. Ajouter $\frac{1}{2}$ ml de H_2SO_4 et renouveler l'évaporation à sec.

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* Si le minerai contient des substances organiques (bitumes, etc. . . .) la prise d'essai devra être préalablement calcinée.

Bibliographie p. 56.

3) Ajouter 2 g ± 0.10 de $KHSO_4$. Fondre sur bec Meker dans le bécher Pyrex tenu au moyen d'une pince métallique, insister sur la fusion jusqu'à transformation presque complète du bisulfate en pyrosulfate.

4) Reprendre par 5 ml d'eau alcoolisée à 5% et 5 ml de solution ferrique F. Couvrir le bécher avec un verre de montre, chauffer au bain de sable doux jusqu'à désagrégation du gâteau de pyrosulfate.

5) Ajouter avec précaution 25 ml ± 1 de solution de carbonate de sodium à 150 g/l (le précipité ferrique doit être persistant après addition de moins des deux tiers de la solution de carbonate. Le pH est alors voisin de 10).

6) Porter les béchers couverts au voisinage de la température d'ébullition pendant environ 15 min, afin de faire floculer l'abondant précipité ferrique.

7) Transvaser quantitativement en ballons jaugés de 50 ml en rinçant à l'eau distillée verres de montre et béchers et en détachant le précipité ferrique adhérant aux parois au moyen d'un agitateur caoutchouté. Faire refroidir et terminer la mise au volume avec H_2O.

8) Filtrer sur sec en éliminant les 5 ou 10 premiers ml.

9) Transférer 5.00 ml de solution filtrée dans des ballons jaugés secs de 25 ml.

10) Ajouter 1 ml ± 0.05 d'acide tartrique à 500 g/l. Agiter avec précaution.

11) Compléter immédiatement au volume, au moyen de la liqueur colorimétrique C.

12) Laisser la température se stabiliser ½ heure environ et colorimétrer à 415 mμ, en cuves couvertes de 3 cm.

13) *Essai à blanc*: suivre intégralement le mode opératoire, sans minerai.

14) *Témoin* 0.50% U_3O_8: opérer comme pour l'essai à blanc, mais ajouter 5 ml de solution étalon d'uranium E_1 entre 4) et 5).

b) *U_3O_8 compris entre* 0.50 *et* 2.5%

Diluer 2 à 5 fois suivant teneur, la solution à colorimétrer au moyen de l'essai à blanc 13) préparé initialement en quantité suffisante.

— dilution 2: mélanger 10.000 ml d'analyse et 10.00 ml d'essai à blanc dans un récipient sec.
— dilution 5: introduire 5 ml de solution à colorimétrer dans un ballon jaugé de 25 ml et compléter au volume avec l'essai à blanc.

c) *Teneurs comprises entre* 2.5 *et* 10% *d'U_3O_8*

Diluer 10 à 20 fois suivant teneur la liqueur carbonique obtenue au stade no. 8, au moyen de la liqueur carbonique à blanc 8) correspondante, préparée initialement en quantité suffisante.

Poursuivre le mode opératoire à partir de 9) sur la solution obtenue.

d) *Teneurs supérieures à* 10%

Modifier le mode opératoire comme suit:

1) 2) 3) Sans modification.

4) Utiliser 20 ml de solution ferrique au lieu de 5.

5) Transvaser en fioles jaugées Pyrex de 2000 ml au lieu de 50, ajouter environ 500 ml d'eau distillée (utilisée en partie pour le rinçage des béchers) puis 50 g de Na_2CO_3 anhydre.

6) Porter au voisinage de la température d'ébullition directement dans les fioles Pyrex de 2000 ml.

7) Faire refroidir et porter au volume avec H_2O.

8) à 12) Pas de modification.

13) *Essai à blanc*: opérer sans minerai dans les mêmes conditions.

14) *Témoin* 20%: ajouter 20 ml de solution étalon E_2 au lieu de 5 ml de E_1, entre les opérations 5) et 6) du présent mode opératoire effectué sans minerai.

Notes

a. La stabilisation de la température est importante pour l'obtention d'une bonne précision relative. Un écart de température de 1°C entre l'analyse et le témoin se traduit par une erreur relative de 0.7% (voir Fig. 5, courbe $D = f(T)$).

b. Il est recommandé de colorimétrer en cuves couvertes afin d'éviter la formation des volutes que peut provoquer une évaporation superficielle du liquide. Attendre 30 secondes environ avant de mesurer la densité optique afin que se résorbent les volutes formées pendant le remplissage des cuves.

Bibliographie p. 56.

c. Dans certains cas spéciaux (matériaux contenant une teneur en béryllium attaquable supérieure à 10%) il peut être nécessaire d'effectuer la colorimétrie immédiatement, un précipité prenant naissance dans la solution au bout de 15 à 30 minutes. On mesurera alors le témoin dans les mêmes délais que l'analyse, afin que sa température soit la même (un léger échauffement se produit lors de l'addition de la liqueur colorimétrique C).

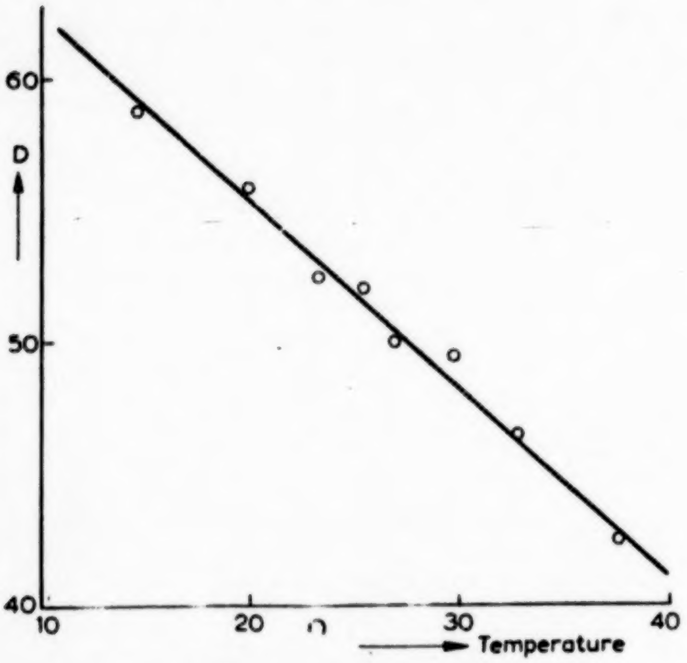

Fig. 5. Influence de la température

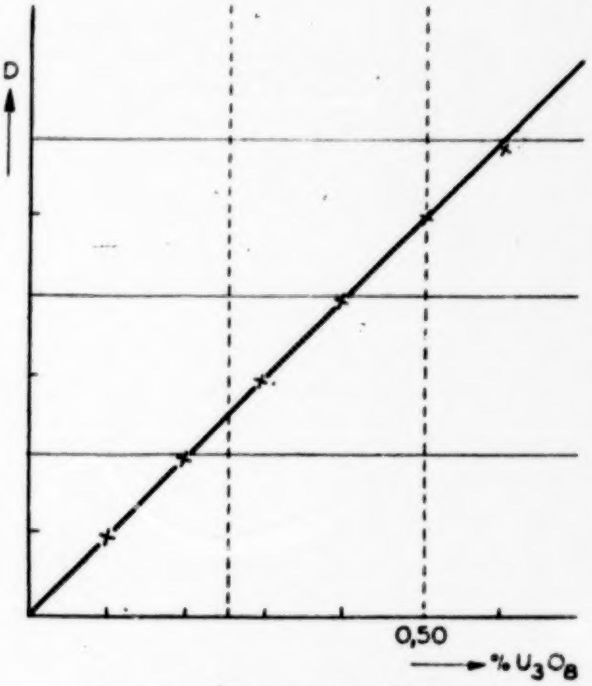

Fig. 6. Étude de la linéarité (mode opératoire total)

d. Dans le cas où l'on désire une forte précision relative sur les hautes teneurs, il convient de combiner volumes et dilutions de façon à obtenir une densité optique comprise entre 0.7 et 1 fois celle du témoin. Un très léger écart à la linéarité (atteignant 1.5% relatif) motive cette recommandation (Fig. 6).

e. Il a été indiqué d'ajouter à la liqueur ferrique F de l'acide phosphorique. Cette addition avait été faite dans l'espoir de supprimer les interférences Zr et Hf avant que soit adoptée l'addition d'acide tartrique. Bien que H_3PO_4 soit très probablement inutile, nous l'avons maintenu dans la composition de F parce que tous les tests d'interférences des autres éléments ont été effectués en sa présence.

f. Le mode d'attaque du minerai que nous indiquons (chauffage et évaporation à sec en présence de H_2SO_4 puis fusion avec $KHSO_4$) réalise une attaque assez énergique. Dans les cas particuliers où l'on sait que le minerai est attaquable par $HClO_4$ et *ne contient pas de fluorures*, on peut se contenter de faire l'attaque directement dans les récipients jaugés Pyrex, à raison de 4 ml de $HClO_4$ dans un ballon de 100 ml, pour une prise d'essai de 500.0 mg de minerai additionnée de (10 ml) de liqueur ferrique F avant l'attaque. On porte et maintient à début de fumées blanches. La reprise par l'eau alcoolisée 10 ml est alors importante dans le cas où l'absence de chrome n'est pas certaine. Ajouter ensuite 50 ml de Na_2CO_3 à 150 g/l et poursuivre à partir de 6).

Pour les minerais particulièrement difficiles à attaquer, on peut, s'ils ne contiennent pas de fluorures (tolérance: $CaF_2 \leqslant 2\%$ du minerai), effectuer une fusion de 2.5 g d'échantillon avec 15 à 20 g de Na_2O_2 dans un *creuset de fer* (et non dans un creuset de nickel). On reprend ensuite par 200 ml d'eau, on acidifie par HCl concentré pour mettre tout l'oxyde de fer en solution, en ajoutant un excès de 10 ml environ. On ajoute 5 ml d'alcool éthylique, puis on fait bouillir une vingtaine de minutes (réduction de Cr^{+6} et destruction de H_2O_2).

On ajoute alors 30 g de Na_2CO_3 anhydre, on porte au voisinage de la température d'ébullition pendant une quinzaine de minutes, on transvase dans une fiole jaugée de 500 ml et on met au volume avec H_2O. Le blanc et le témoin sont évidemment préparés en conséquence, le témoin 0.5% U_3O_8 par addition de 5 ml de solution E_2 à un essai à blanc avant l'addition du carbonate. Le mode opératoire se continue ensuite sans autres modifications à partir de 9).

5. ÉTUDE ET ÉLIMINATION DES INTERFÉRENCES

Une étude préliminaire a montré que les éléments susceptibles d'interférer fortement avec la mesure de l'uranium étaient les suivants:

Fe^{+3}, Fe^{+2}, Cr^{+3}, Cr^{+6}, Zr, Hf, Th, PO_4^{-3}, AsO_4^{-3}, V^{+5}, F^- ainsi que Au et Pt.

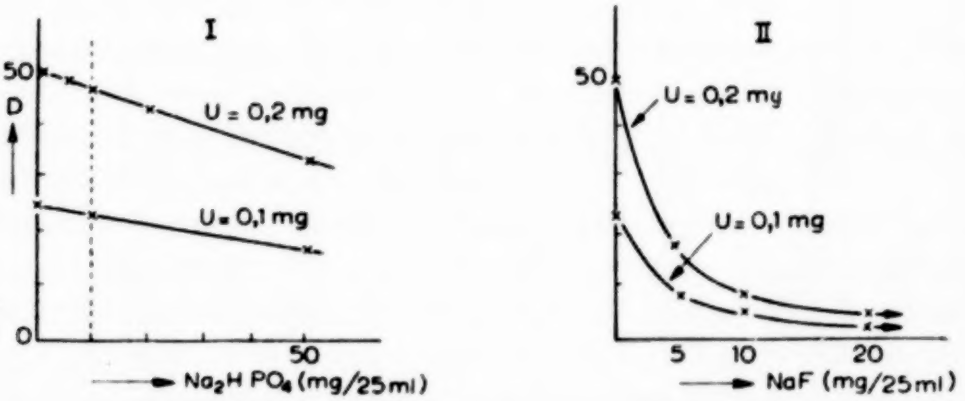

Fig. 7. I Influence des phosphates
II Influence des fluorures

Les principaux mécanismes d'interférence sont:

a) Formation d'un complexe absorbant à 4000 Å avec le dbm: cas de Zr, Hf, Th, Fe^{+3}.
b) Formation d'un complexe absorbant à 4000 Å avec l'EDTA: cas de Fe^{+2}, Cr^{+3}.
c) Formation d'un complexe incolore avec U, s'opposant au développement total de la coloration U + dbm: cas de PO_4^{-3}, AsO_4^{-3}, F^- (Fig. 7).

Les deux premiers types d'interférence conduisent à une erreur par excès, affectant aussi bien les minerais contenant de l'uranium que les minerais stériles.

Le troisième type ne provoque pas d'erreur sur les stériles, mais conduit à une erreur par défaut sur les échantillons contenant de l'uranium (Fig. 7).

Certains éléments semblent interférer par plusieurs mécanismes, tels V^{+5} tandis que Au, Pt, Cr^{+6} n'interviennent probablement que par leur coloration propre.

1° L'interférence de F^- est aisément éliminée lorsque l'attaque de l'échantillon comporte une ou deux évaporations à sec en présence de H_2SO_4.

2° Les interférences de Zr, Hf, Th ainsi que le montrent les courbes (Fig. 8) sont pratiquement éliminées pour Th et très diminuées pour Hf et Zr lorsque la mesure est effectuée à 415 mμ au lieu de 400. Ces deux dernières interférences sont encore très fortement réduites par addition d'un peu d'acide tartrique à la prise d'essai contenant l'uranium avant l'introduction de la liqueur colorimétrique C. L'acide tartrique, complexant l'uranium, doit être utilisé en quantité limitée: 1 ml d'acide à 500 g/l pour un volume total de 25 ml. Dans ces conditions, la sensibilité de la mesure n'est que peu diminuée (de 1/20 environ).

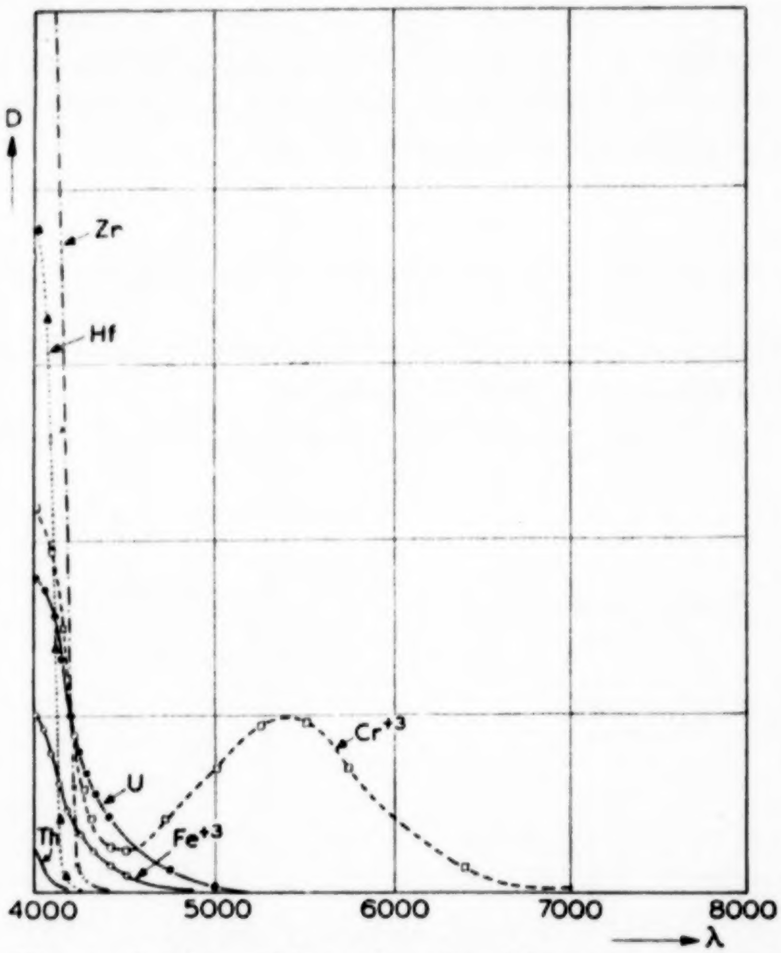

Fig. 8. Courbes d'absorption des éléments interférents

3° Les interférences de Fe^{+3} et Cr^{+3} (Fig. 8) ne peuvent être éliminées en passant à une autre valence. En ce qui concerne Cr^{+3}, l'interférence initialement très faible, augmente avec le temps, tandis que la solution passe d'une teinte presque insensible à un violet pourpre assez intense. En ce qui concerne Fe^{+3}, il y a aussi évolution de la teinte du jaune orangé au jaune pur.

Pour éliminer ces éléments, nous avons mis au point un mode opératoire simple de séparation par le carbonate de sodium. Une étude détaillée dont les résultats sont donnés plus loin, a montré que, contrairement à des idées généralement reçues l'entraînement de l'uranium par les oxydes ou carbonates précipités était absolument insignifiant, même avec des rapports Fe/U dépassant 1000, tout au moins dans les conditions opératoires qui sont décrites. Il en est pratiquement de même pour la plupart des autres carbonates ou hydroxydes, dont les plus adsorbants seraient ceux de Ni, Co, Sr. Encore faut-il noter que même dans des minerais contenant de 10 à 20% de ces éléments, 0.5% d'uranium peuvent être déterminés à 1 ou 2% relatifs près, (voir paragraphe sur les interférences).

Bibliographie p. 56.

4° En ce qui concerne les interférences de PO_4^{-3} et AsO_4^{-3} nous avons mis à profit le fait que la précipitation de Fe par le carbonate n'entraîne pratiquement pas d'uranium pour ajouter systématiquement aux minerais une importante quantité d'un sel de fer. Dans ces conditions, lors de la précipitation par Na_2CO_3, PO_4^{-3} et AsO_4^{-3} sont éliminés sous forme de sels ferriques insolubles et les interférences sont supprimées même pour des teneurs correspondant à 100% de phosphate disodique ou à 25% de As dans le minerai.

5° Les interférences de l'or et du platine ne sont pas supprimées par le mode opératoire; toutefois, les quantités tolérables pour ne pas dépasser une erreur absolue de 0.005% sur l'uranium, étant de 10.000 g/t pour Au et de 20.000 à 30.000 g/t pour Pt, il n'y a pas lieu d'en tenir compte dans les cas usuels où de telles teneurs en métaux précieux ne se rencontrent pas. De plus, le mode opératoire ne provoquerait probablement pas l'attaque de ces éléments, qui, même présents en assez fortes teneurs pourraient ne pas interférer.

Dans certains cas, notamment si le minerai est soumis à une attaque perchlorique, le chrome passe à la valence +6 et n'est pas éliminé lors de la précipitation des hydroxydes et carbonates par Na_2CO_3. Pour éviter l'interférence qui en résulterait, le mode opératoire comporte une reprise par l'eau alcoolisée à 5%, ce qui assure la réduction de Cr^{+6} en Cr^{+3} coprécipitant avec le fer.

6° L'expérience montre que, lors de la séparation au carbonate, Zr, Hf et Th restent en grande partie dans la phase liquide et accompagnent l'uranium. Il en résulte que l'addition d'acide tartrique mentionnée dans la 2ième partie de ce paragraphe reste indispensable, ainsi que le choix de $\lambda = 415$ mμ.

7° Nous prévoyons comme mode habituel d'attaque du minerai la fusion avec le bisulfate de potassium. Pour éviter que l'addition d'acide tartrique (alinéa 2) n'entraîne une précipitation de bitartrate de potassium, on ajoute un peu de $HClO_4$ qui précipite la majeure partie du potassium qui est ainsi séparé en même temps que les carbonates ou hydroxydes lors de la filtration unique que comporte la méthode.

Les essais d'interférence ont été effectués selon les modes opératoires suivants:

a) 1. Introduction dans un ballon jaugé de 50 ml de la quantité voulue d'interférent pris sous forme de sel solide ou sous forme de solution; addition éventuelle d'uranium; introduction de 5 ml de liqueur ferrique F et de 4 ml de $HClO_4$.
   2. Chauffage sur Meker jusqu'au début de fumées perchloriques.
   3. Reprise par 5 ml d'alcool à 5% et un peu d'eau; addition de 25 ml de solution de carbonate de sodium à 150 g/l et poursuite du mode opératoire indiqué pour les minerais depuis 8).

b) Mode opératoire indiqué pour les minerais suivi intégralement. Les interférents en solution et l'uranium étant préalablement évaporés à sec dans les béchers.

Le mode opératoire comportant une fusion au bisulfate n'a été appliqué qu'à un nombre restreint d'éléments; ceux qui semblaient susceptibles de se comporter différemment en présence de $HClO_4$ ou de $KHSO_4$.

Ta_2O_5, Nb_2O_5, TiO_2, WO_3 attaqués par $KHSO_4$ et non par $HClO_4$.

Ce, Fe, As, Sb, Te aboutissant à des valences différentes.

Pb, Ca, Sr, Ba conduisant à des sulfates insolubles, mais à des perchlorates solubles.

Les résultats obtenus sont résumés par le Tableau I.

TABLEAU I

Interférent ajouté	*Uranium trouvé*		*Notes*
	U introduit = 0.00%	*U introduit = 0.50%*	
50% LiO_2	−0.005	0.50	
50% Na_2SO_4	0	0.50	
50% KCl	0	0.51	
50% Cs	+0.01	0.51	
50% Cu	0.005	0.51	Note 4
50% Cu	0	0.50	fusion $KHSO_4$
50% Ag	0.01	0.505	
2% Au	0.03	0.515	
50% $Be(OH)_2$	0.03	0.515	Note 1
20% $Be(OH)_2$	0.015	0.50	
10% $Be(OH)_2$	0	0.49	
50% Mg	0.005	0.505	
50% Ca	0	0.49	
50% Sr	0	0.31	Note 2
25% Sr	0	0.42	
10% Sr	0	0.46	
5% Sr	0	0.495	
50% Ba	0	0.48	
25% Ba	0	0.505	
50% Zn	0.00	0.50	
50% Cd	0.00	0.505	
50% Hg	0.01	0.51	
50% B_2O_3	0.03	0.52	Note 3
25% B_2O_3	0.01	0.51	
100% Al_2O_3	0	0.40	
50% Al_2O_3	0	0.49	Note 2
50% Ga_2O_3	−0.01	0.49	
25% In_2O_3	0.00	0.49	
25% Tl	0.005	0.505	
25% Sc_2O_3	0.00	0.48	
50% Y_2O_3	0.01	0.50	
50% La_2O_3	0.005	0.50	
50% Ce_2O_3	0	0.505	
100% SiO_2	0	0.505	
50% GaO_2	−0.01	0.495	
50% Sn	0.005	0.50	
50% TiO_2	−0.005	0.48	
25% ZrO_2	0.01	0.51	Note 5
10% ZrO_2	0	0.50	
10% Hf	0	0.50	
60% ThO_2	0.03	0.53	Note 5
30% ThO_2	0	0.52	
15% ThO_2	0.005	0.51	
50% Pb	0	0.47	
25% Pb	0	0.48	
10% Pb	0	0.49	
50% P_2O_5	0	0.47	
25% P_2O_5	0	0.51	
10% P_2O_5	0	0.505	
25% V_2O_5	0.03	0.53	Note 6
25% V_2O_5	−0.005	0.53	fusion $KHSO_4$
10% V_2O_5	0.01	0.505	
10% V_2O_5	+0.01	0.51	fusion $KHSO_4$
50% Nb_2O_5	−0.01	0.49	
50% Ta_2O_5	−0.01	0.49	
50% NH_4	0.005	0.51	
50% As	+0.02	0.52	
25% As	−0.005	0.50	

TABLEAU I (suite)

Interférent ajouté	*Uranium trouvé* *U introduit* = 0.00%	*Uranium trouvé* *U introduit* = 0.50%	*Notes*
25% Sb	—0.01	0.505	
50% Bi	0.00	0.51	
10% Cr	—0.005	0.51	
50% MoO_3	+0.01	0.485	
50% WO_3	0.00	0.495	
25% Se	—0.01	0.515	
50% Te	+0.005	0.51	
4% Te	—0.005	0.505	
50% Mn	—0.005	0.505	
4% Re	0.005	0.505	
99% NaF	0	0.515	
50% KCl	0	0.50	
50% NaBr	0.005	0.51	
50% KI	0.02	0.50	
25% KI	0	0.505	
50% Fe	—0.005	0.505	fusion $KHSO_4$
50% Fe	—0.005	0.51	attaque $HClO_4$
50% Co	0	0.43	Note 2
25% Co	0	0.495	
10% Co	0	0.50	
50% Ni	0	0.30	Note 2
25% Ni	0	0.48	
10% Ni	0	0.50	
2% Pt	0	0.50	
10% Pd	0	0.495	
4% In + 4% Se + 4% MoO_3 + 4% WO_3 + 4% GeO_2	—0.005	0.51	
4% Tl + 4% Sn + 4% Bi + 4% Cd + 4% Ag + 4% Hg	0	0.49	

Note 1

En présence de 50% de $Be(OH)_2$, un précipité se forme au bout d'une dizaine de minutes dans la liqueur à colorimétrer. Il faut donc effectuer la mesure rapidement. Pour $Be(OH)_2$ = 20%, le précipité ne se forme qu'après 20 minutes environ et pour $Be(OH)_2$ = 10%, on dispose d'environ 45 minutes.

Note 2

L'erreur par défaut provoquée par les fortes teneurs en Sr, Co, Ni n'est pas due à une consommation de dbm par une fraction de l'élément non précipitée par Na_2CO_3, mais à une rétention d'uranium par le précipité d'hydroxyde ou de carbonate. Il semble que cette rétention soit supprimée pour les teneurs pas trop élevées à la faveur d'une influence de la coprécipitation du fer. L'addition d'une quantité supplémentaire d'uranium après la filtration des carbonates ou hydroxydes se traduit par une augmentation parfaitement normale de la densité optique.

Bibliographie p. 56.

Note 3

L'interférence légère des fortes quantités de B_2O_3 est probablement due à une précipitation incomplète du fer.

Note 4

La précipitation de Cu par Na_2CO_3 n'est pas totale. Les liqueurs conservent une teinte bleue (verte en présence d'uranium), qui ne nuit pas à la mesure à 415 mμ.

Note 5

Zr et Hf, en l'absence d'acide tartrique, présentent une absorption très intense à 4000Å. Ceci pourrait faire la base d'une colorimétrie de Zr et Hf. Les sensibilités et les courbes sont beaucoup plus différentes pour Zr et Hf que dans les colorimétries classiques de ces éléments.

En ce qui concerne Th, il y aura lieu de faire une correction de 0.01% en U pour 20% de ThO_2, soit 0.05% pour 100% de ThO_2.

Note 6

En présence de fortes teneurs en V_2O_5, une intense coloration jaune se développe lors de l'addition du ml d'acide tartrique à 500 g/l. Cette teinte disparait lorsqu'on ajoute la liqueur C.

Note 7

L'interférence de Sb, pratiquement nulle pour 25%, devient forte pour 50%. Dans le cas d'une attaque perchlorique du minerai, il est préférable d'ajouter $FeCl_3$ (liqueur F) avant l'attaque perchlorique. L'expérience montre qu'alors l'interférence Sb ne se manifeste que pour des teneurs plus élevées. Dans le cas d'une fusion avec $KHSO_4$, on n'a pas fait d'essais sur les teneurs supérieures à 25% de Sb.

Note 8

L'attaque perchlorique simple ne suffit pas à éliminer HF. En effectuant les 2 évaporations sulfuriques préconisées dans le mode opératoire, on a toute sécurité. La présence de moins de 2% de CaF_2 dans le minerai n'entraîne toutefois qu'une erreur négligeable même par attaque perchlorique.

Note 9

Les éléments des terres rares autres que Sc, Y, La et Ce n'étant pas à notre disposition n'ont pu être essayés. Il en est de même pour les éléments de la famille du platine autres que Pt et Pd.

Note 10

Les nitrates et sulfates n'interfèrent pas.

6. CONCLUSIONS

Le mode opératoire proposé permet le dosage de l'uranium dans des conditions très générales, en présence des impuretés les plus variées.

Si on tolère une erreur absolue ± 0.01% d'uranium sur un échantillon à 0.50%, les seuls éléments dont la teneur dans le minerai ne doive pas dépasser 10% sont: Sr, Ni, Au et Pt.

Bibliographie p. 56.

Dans le cas du dosage des hautes teneurs, le rapport uranium/impureté devient évidemment beaucoup plus favorable et on peut considérer que la méthode est tout-à-fait générale. Les quantités tolérables d'impuretés ne sont plus limitées si on suit le mode opératoire indiqué pour les teneurs supérieures à 10% puisqu'on peut alors multiplier par 20 les tolérances relatives au cas des minerais contenant 0.50% d'uranium.

En ce qui concerne les très basses teneurs, on peut envisager la possibilité de mettre au point un procédé permettant de multiplier par 10 ou 20 la sensibilité en terminant sur une aliquote plus importante et en effectuant une extraction par solvant. Une étude préliminaire nous a en effet montré que le complexe (U + dbm) était extractible en présence de pyridine par de très nombreux solvants organiques (alcool isoamylique, chloroforme, acétate d'isoamyle, oxyde d'isopropyle, cyclohexanone, hexane, thiophène, etc . . .). La légère interférence du thorium (erreur de 0.01% d'uranium pour 20% de ThO_2), est alors supprimée, Th restant dans la phase hydropyridinique.

Que Monsieur BLAGOJE ZOGOVIĆ de *l'Institut de Recherches Géologiques, Minières et Technologiques (Belgrade)* qui a participé à la première phase des recherches, et Monsieur KHOI VO DINH, qui a pris une part très importante à la mise au point de la méthode, trouvent ici l'expression de notre gratitude.

RÉSUMÉ

Une méthode de dosage colorimétrique de l'uranium par le dibenzoylméthane est étudiée et décrite.

Le complexe est formé en milieu hydropyridinique en présence d'EDTA et d'acide tartrique, la densité optique est mesurée à 415 $m\mu$.

La loi de Beer s'applique et la sensibilité est de 0.005% d'uranium dans le minerai.

La méthode opératoire comporte une filtration unique et est applicable en présence des impuretés les plus variées, y compris Mo, W, V, Ce, Th, F et P.

Aucun élément ne gène la détermination des teneurs supérieures à 5%. La détermination des teneurs inférieures à 0.50% n'est entachée d'une erreur absolue supérieure à 0.02% qu'en présence de plus de 1% d'or, 2% de platine, 10% de strontium attaquable.

Le mode opératoire a été appliqué avec toute satisfaction à l'analyse de pechblende, autunite, thorianite, colombite, urano-thorianite, tantalite, carnotite pour des teneurs allant de 0.05 à 25% d'uranium.

SUMMARY

A colorimetric method for the determination of uranium by means of dibenzoylmethane has been studied and described.

The complex is formed in aqueous pyridine in the presence of EDTA and tartaric acid; the optical density is measured at 415 $m\mu$.

Beer's Law applies; the sensitivity amounts to 0.005% uranium in the mineral.

The method involves only one filtration and can be used in the presence of various impurities including Mo, W, V, Ge, Th, F and P.

With a uranium content of more than 5% no single element disturbs the determination. With a content of less than 0.5% the absolute error amounts to more than 0.01% only in the presence of 1% gold, 2% platinum or 10% soluble strontium.

The method described has been applied with completely satisfactory results to the analysis of pitchblende, antunite, thorianite, columbite, urano-thorianite, tantalite and carnotite containing from 0.05 to 25% uranium.

Bibliographie p. 56.

ZUSAMMENFASSUNG

Eine kolorimetrische Bestimmungsmethode von Uran mit Hilfe von Dibenzoylmethan wird studiert und beschrieben.

Der Komplex wird in wässrigem Pyridin in Gegenwart von EDTA und Weinsteinsäure gebildet; die optische Dichte wird bei 415 mμ gemessen.

Das Beer'sche Gesetz gilt; die Empfindlichkeit beträgt 0.005% Uran im Mineral.

Das Verfahren umfasst nur eine Filtration und kann in Gegenwart der verschiedensten Verunreinigungen mit Inbegriff von Mo, W, V, Ce, Th, F und P angewendet werden.

Kein einziges Element stört die Bestimmung bei Gehalten die höher sind als 5%. Bei Gehalten die niedriger sind als 0.50% beträgt der absolute Fehler nur in Gegenwart von 1% Gold, 2% Platin oder 10% löslichem Strontium, mehr als 0.02%.

Das beschriebene Verfahren wurde zu vollster Zufriedenheit auf die Analyse von Pechblende, Autunit, Thorianit, Columbit, Urano-Thorianit, Tantalit und Carnotit mit Urangehalten von 0.05 bis 25% angewendet.

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DIRECT SPECTROPHOTOMETRIC DETERMINATION OF THORIUM WITH SPADNS*

by

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INTRODUCTION

Since the thorium ion is colourless and yields but few coloured derivatives, direct colorimetric methods for the element have only been recently developed. Among the indirect colorimetric methods for thorium, mention may be made of pararsonic acid (*p*-dimethylaminoazophenylarsonic acid) method[1], reduction of thorium iodate[2] and of thorium *m*-nitrobenzoate[3]. In another method[4], the determination is based upon the precipitation of thorium oxalate, the subsequent reduction of the excess oxalate with potassium permanganate and measurement of the excess manganate ion.

The first direct spectrophotometric method for determining thorium in the range 5 to 80 micrograms, was developed by THOMASON, PERRY AND BYERLY[5], using APANS (1-*o*-arsenophenylazo-2-naphthol-3,6-disulphonic acid). A rapid and accurate method for the determination of thoria in monazite sands using the reagent has also been described by BANKS AND BYRD[6]. Titanium, zirconium and ferric iron are found to interfere during the estimation of thorium. RAO AND RAO[7] have recently reported the use of nitroso-R-salt for the direct colorimetric estimation of thorium and Alizarin Red S has also been recommended by MURTHY AND RAO[8] for the purpose.

In view of the need for a rapid method for the determination of trace amounts of thorium, a method has been developed for the micro determination of thorium even as little as $0.04\,\gamma$ in 25 ml of final volume and it consists of adjustment of pH, addition of SPADNS (2-*p*-sulphophenylazo-1,8-dihydroxynaphthalene-3,6-disulphonic acid), dilution to volume and measurement of optical density in a Unicam SP 600 spectrophotometer *versus* a reference solution of the organic reagent. The method is based on the fact that thorium forms a blue-violet soluble complex with the reagent which is stable in acid medium. The method offers advantage as the reagent can be easily prepared by diazotizing sulphanilic acid and then coupling with chromotropic acid (1,8-dihydroxynaphthalene-3,6-disulphonic acid).

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* A note on the subject was published in *Science and Culture (India)*, 20 (1955) 611. June, 1955.

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References p. 61.

EXPERIMENTAL

Synthesis of the organic reagent. Pure 2-p-sulphophenylazo-1,8-dihydroxynaphthalene-3,6-disulphonic acid in the form of its sodium salt (SPADNS) was prepared according to the method outlined by the author[9].

Materials. A standard solution of thorium was prepared by dissolving 5.95 g of chemically pure thorium nitrate tetrahydrate (Merck's sample) in distilled water and diluting to 250 ml. This solution containing 8.24 mg of thorium per ml was standardized by evaporating 5 ml aliquots to dryness in a platinum crucible and igniting to thoria at 1000° C to a constant weight. This solution was further diluted to obtain solutions containing different microgram amounts of thorium per ml. All other chemicals used in this work were pure Merck's samples.

Apparatus and technique. One Unicam SP 600 spectrophotometer with 1 cm path length cells was used for all measurements. All solutions were diluted to a final volume of 25 ml before being transferred to the absorption cells. — pH was measured with a Cambridge bench type meter and adjusted to the proper value by adding either dilute nitric acid or ammonia or sodium acetate-hydrochloric acid buffer.

Absorption curves. The measurement of the spectral absorption of a water solution of the organic reagent (A in Fig. 1) and of a similar solution containing thorium (B in Fig. 1) indicated a shift of the absorption band towards longer wavelengths upon the addition of thorium. These measurements were done using distilled water as the reference solution. When the solution of the reagent plus thorium was measured against the solution of the reagent, B-A (C in Fig. 1), the predicted curve was obtained showing a maximum absorption at 570-580 mμ. The data are plotted in Fig. 1.

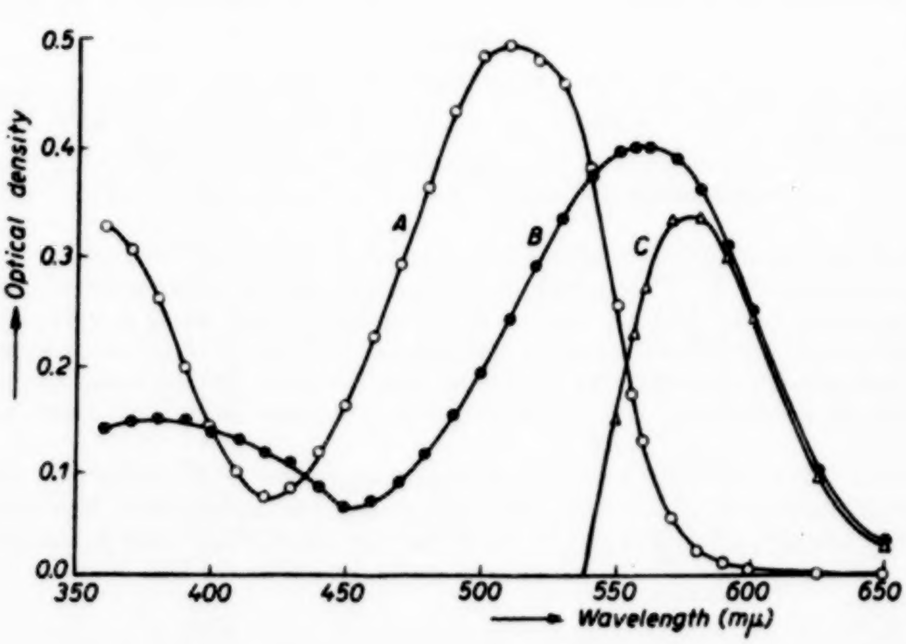

Fig. 1. Absorption spectra of SPADNS.
A. Reagent against water.
B. Reagent plus thorium against water.
C. Reagent plus thorium against reagent.

Effect of various amounts of reagent. The absorption of a series of solutions of pH (3 approx.), each containing 4 γ Th per ml but with varying amounts of reagent was measured to determine a suitable concentration of the reagent. Results have been plotted in Fig. 2 which indicates that 3.0 ml of an aqueous solution of 0.1% organic reagent is sufficient to complex 0.004 mg of thorium in 25 ml volume.

Effect of pH. A series of solutions containing thorium and the organic reagent was adjusted to various pH values with hydrochloric acid. Each of these was measured against distilled water as the reference solution. Between a pH of 2.6 and 3.6, the absorption remained constant and above 3.6, the absorption decreased rapidly, as indicated in Fig. 3. A series of reference solutions containing only the reagent at various pH values was measured against distilled water. The data given in Table I show that in the pH range 2.6-3.6, the maximum error due to variation in pH is within 1% and the reagent is quite stable in acid medium.

Effect of time. No change in optical densities was noted for 24 hours after preparation of the Th-SPADNS complex as well as the reagent blank and thus, the system was sufficiently stable for quantitative determinations.

Effect of temperature. Over a period of 24 hours under laboratory conditions of light and temperature (*i.e.* temperature in the range 20-30° C), the optical density of a solution of thorium-SPADNS complex remained almost constant.

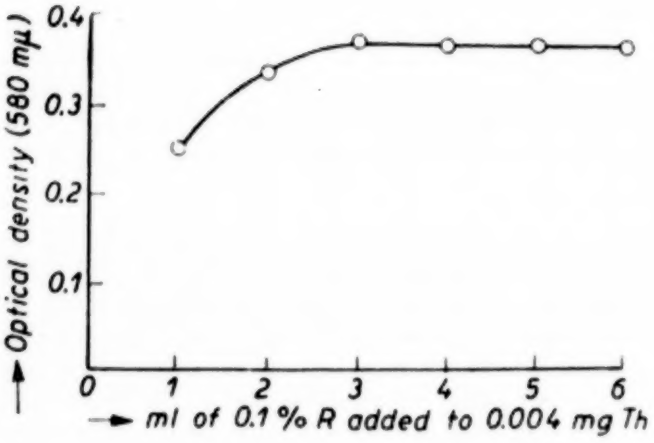

Fig. 2. Effect of reagent.

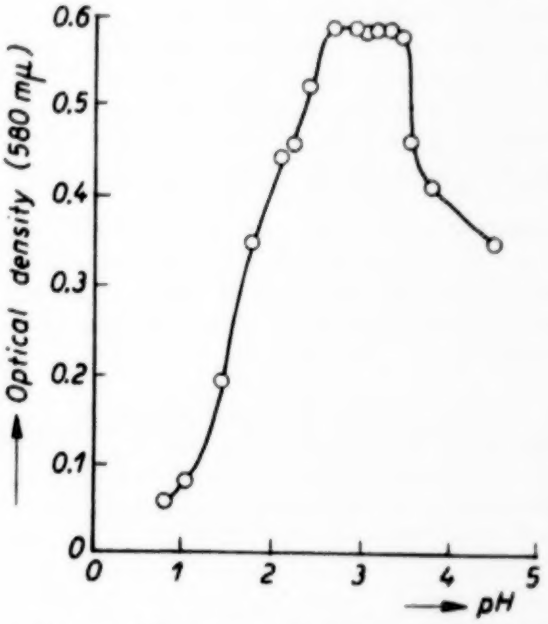

Fig. 3. Variation of optical with pH.

TABLE I

VARIATION OF OPTICAL DENSITY WITH pH

3 ml of 0.1% reagent in water + 7 μg of thorium measured *vs* water		3 ml of 0.1% reagent diluted to 25 ml distilled water measured *vs* water	
pH	*Optical density*	*pH*	*Optical density*
0.80	0.057	0.80	0.055
1.08	0.078	1.04	0.054
1.46	0.195	1.40	0.060
1.76	0.348	1.75	0.055
2.10	0.444	2.13	0.052
2.20	0.458	2.20	0.052
2.40	0.521	2.42	0.055
2.66	0.588	2.48	0.048
2.94	0.588	2.62	0.055
3.00	0.580	2.70	0.050
3.10	0.588	2.93	0.055
3.16	0.588	3.10	0.068
3.26	0.580	3.76	0.071
3.40	0.578	4.25	0.055
3.51	0.578	4.90	0.055
3.76	0.460	5.18	0.056
4.16	0.411		
4.48	0.355		

References p. 61.

Beer's law. The coloured solution obey's Beer's law giving a standard curve that is a straight line (*vide* Fig. 4) passing through the origin with an optical density of 0.334 for 4 γ of thorium.

Sensitivity. Sensitivity of the colour reaction is either 0.04 γ Th per cm^2 (practical) or 0.012 γ Th per cm^2 (according to Sandell's definition).

Experimental procedure. Aliquots of 0.5, 1.0, 1.5 . . . 6 ml of thorium standard, which contained 0.8 γ of thorium per ml were pipetted into separate 25 ml volumetric flasks. To each flask, were then added, 5 ml of 0.01*N* hydrochloric acid to maintain the desirable pH and 3 ml of 0.1% SPADNS reagent solution. These samples were diluted to 25 ml with distilled water. A reference was prepared by diluting 5 ml of 0.01*N* HCl and 3 ml of 0.1% reagent to 25 ml with distilled water. The samples were then transferred to the absorption cells and their optical densities were measured in a Unicam SP 600 spectrophotometer.

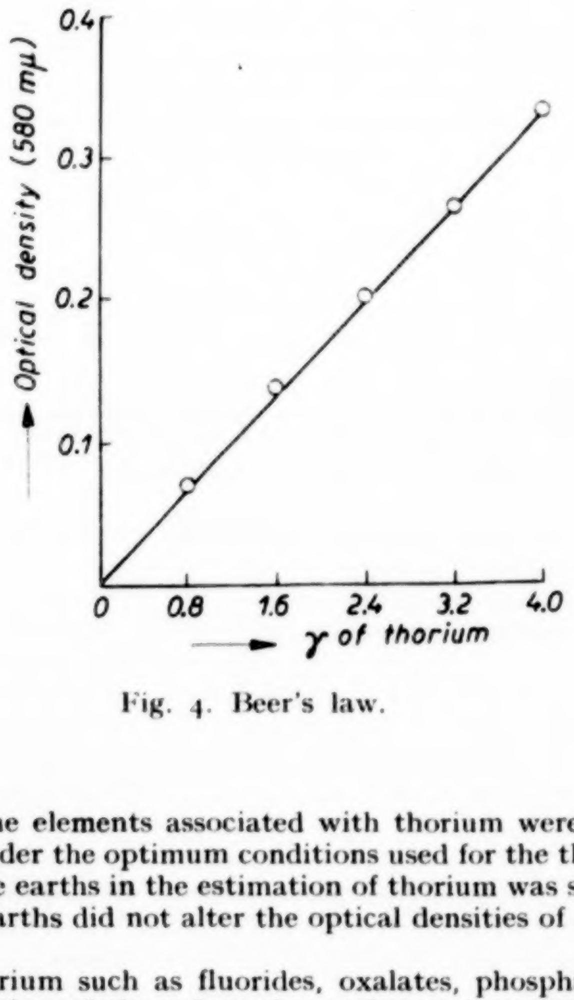

Fig. 4. Beer's law.

Interference. Nearly all the elements associated with thorium were tested to determine their behaviour with SPADNS under the optimum conditions used for the thorium-SPADNS reactions. The interference of the cerite earths in the estimation of thorium was studied. The results showed that the addition of cerite earths did not alter the optical densities of neither the reagent nor the thorium complex.

Anions that complex thorium such as fluorides, oxalates, phosphates and large amounts of sulphates inhibit the formation of the coloured complex and must therefore be absent.

As the reagent gives a faint purple colour with uranyl ion, spectral absorptions of a water solution of the reagent and that of another containing uranium at 580 mμ were studied, and it was found that the absorption of the reagent was greater than that of the uranium complex. It is evident therefore, that moderate amounts of uranium do not interfere with the estimation of thorium.

Since zirconyl ion gives a crimson-pink colour with SPADNS with absorption spectra closely comparable with that given by thorium ion, the presence of zirconium interferes seriously during the estimation of thorium. Thus, the work on the spectrophotometric estimation of zirconium with the reagent has been taken up separately[10].

Composition of the coloured complex of thorium and SPADNS

The empirical formula of the coloured complex of thorium was determined by adopting the "slope ratio method"[11].

For the study of the complex, two series of solutions were prepared. In one series, the concentration of thorium was varied in the presence of constant excess of SPADNS; in the other, SPADNS was variable and thorium was the constant component. The pH of the solutions was adjusted to the desired value by using $0.01\,N$ HCl as the solvent of the reagent and thorium as well as the diluting liquid.

Optical density measurements at the wavelength of maximum absorption for thorium complex were made within 20 minutes after preparing the solutions. The slope ratio obtained in Fig. 5 is 1 : 0.8. Giving allowance for experimental error, the above ratio suggests a 1 : 1 complex for thorium with the reagent. The results are tabulated in Table II.

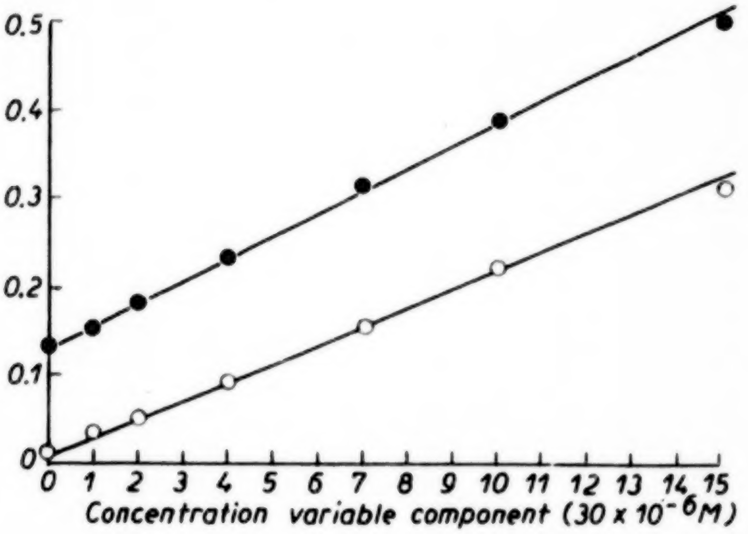

Fig. 5 Slope ratio: blue-violet complex of thorium and SPADNS, pH 2.2, 580 mμ.
○ Reagent varying
● Thorium varying
Constant component $30 \cdot 10^{-5}M$

TABLE II

SLOPE RATIO OF THORIUM COMPLEX

ml	*Optical density*
$\text{Th}(30 \cdot 10^{-5}M)$ fixed, $\text{R}(30 \cdot 10^{-6}M)$ varying	
0	0.009
1	0.035
2	0.046
4	0.090
7	0.156
10	0.222
15	0.315
$\text{R}(30 \cdot 10^{-5}M)$ fixed, $\text{Th}(30 \cdot 10^{-6}M)$ varying	
0	0.134
1	0.157
2	0.181
4	0.232
7	0.314
10	0.385
15	0.502

ACKNOWLEDGEMENTS

The author's grateful thanks are due to Prof. P. RÂY for his kind advice and for providing all laboratory facilities and to (late) Dr. A. K. MUKHERJEE, Mr. J. XAVIER and Mr. A. K. CHAKRAVORTY, for their help in various directions.

SUMMARY

A direct spectrophotometric method is described for the determination of thorium using SPADNS as the reagent. The method is sensitive and quantities as small as 0.04 γ of thorium can be estimated. Moderate amounts of uranium and rare earths do not interfere. The stoichiometric composition of the coloured complex has been determined spectrophotometrically by the 'slope ratio method'.

RÉSUMÉ

Une méthode spectrophotométrique est décrite pour le dosage du thorium au moyen de l'acide 2-(p-sulfophénylazo)-1,8-dihydroxynaphtalène-3,6-disulfonique (SPADNS) La méthode est sensible et des quantités allant jusqu'à 0.04 γ de thorium peuvent être dosées. Des quantités modérées d'uranium et de terres rares ne gênent pas. La composition stoechiométrique du complexe coloré a pu être déterminée spectrophotométriquement.

ZUSAMMENFASSUNG

Eine direkte spektrophotometrische Methode zur Bestimmung von Thorium mit Hilfe von 2-*p*-Sulfophenylazo-1,8-dihydroxynaphtalen-3,6-disulfonsäure (SPADNS) wird beschrieben. Die Methode ist empfindlich; es können Thoriummengen bis zu 0.04 γ bestimmt werden. Nicht all zu grosse Mengen von Uran und seltenen Erden stören nicht. Die stöchiometrische Zusammensetzung des gefärbten Komplexes wurde spektrophotometrisch ermittelt.

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DIRECT SPECTROPHOTOMETRIC DETERMINATION OF ZIRCONIUM WITH SPADNS*.

by

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INTRODUCTION

Although a systematic investigation on the suitability of 2,4-dichlorophenoxyacetic acid (2,4-D), diphenic acid and versene for the macro determination of zirconium has been recently carried out by the author[1-3], the situation is far from satisfactory with respect to the determination of microgram amounts of the element.

Owing to the need for rapid accurate micro methods for the determination of zirconium, the question of the development of colorimetric methods for the element attracted the attention of various workers in the analytical field. LIEBHAFSKY AND WINSLOW[4] used alizarin, quinalizarin and purpurine for the colorimetric determination of the metal. Although alizarin (or alizarin Red S) is considered to be the most important colorimetric reagent for zirconium, the colour reaction is not too sensitive. Pararsonic acid (or *p*-dimethylaminoazophenylarsonic acid) has also been utilized by a number of workers[5-7] for the purpose. Their procedures are indirect because the light absorption measurements being made on the dye solution obtained by decomposing the zirconium-azo-arsonate with ammonia. Other spectrophotometric reagents like Thoron (APANS)[8], quercetin[9] etc. for zirconium are also mentioned in the literature.

The thorium-complexing agent[10] 2-*p*-sulphophenylazo-1,8-dihydroxynaphthalene-3,6-disulphonic acid (SPADNS), has been successfully utilized by the author for the direct spectrophotometric determination of microgram amounts of zirconium. The method is based on the fact that zirconium forms a crimson-pink soluble complex with SPADNS which is stable in acid medium. The procedure developed for the micro determination of zirconium in the range 7-56 γ ZrO_2 in 25 ml of final volume involves the adjustment of pH, addition of the organic reagent, dilution to volume and measurement of optical density in a Unicam SP 600 spectrophotometer *versus* a reference solution of the reagent.

EXPERIMENTAL

Materials. A standard stock solution of zirconium nitrate was prepared in 0.01 *N* hydrochloric acid and standardized by evaporation and ignition to the oxide. The zirconium concentration of the solution was 0.00356 g per ml. This solution was further diluted with 0.01 *N* HCl in order to have microgram amounts of zirconium per ml. — Pure SPADNS was prepared as before (loc.cit.).

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* A note on the topic was published previously in *Naturwissenschaften*, 7 (1955) 177.

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Apparatus and technique. One Unicam SP 600 spectrophotometer with 1 cm path length cells was used for all measurements. All solutions were diluted to a final volume of 25 ml before being transferred to the absorption cells. pH was measured with a Cambridge bench type meter and adjusted to the proper value by adding 0.01N hydrochloric acid.

Absorption curves. Like thorium (loc.cit.), the measurement of the spectral absorption of a water solution of the organic reagent (A in Fig. 1) and of a similar solution containing zirconium (B) indicated a shift of the absorption band toward longer wavelength upon the addition of zirconium. These measurements were done using distilled water as the reference solution. When the solution of the reagent plus zirconium was measured against the solution of the reagent, B-A (C in Fig. 1), the curve obtained showed the maximum absorption at 580 mμ like thorium. The data are plotted in Fig. 1.

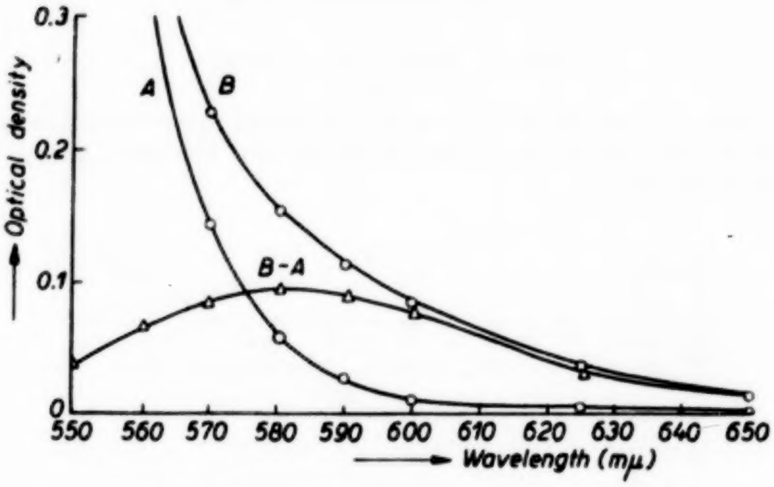

Fig. 1. Absorption spectra of SPADNS
A. Reagent against water.
B. Reagent plus zirconium against water.
B-A. Reagent plus zirconium against reagent.

Effect of variation of reagent. The optical density of a series of solutions in 0.5N HCl, each containing 40 γ zirconium but with varying amounts of reagent was measured to determine the effective concentration of the reagent. Results given in Table I show that 3.0 ml of an aqueous solution of 0.1% reagent is sufficient to complex 40 γ zirconium.

TABLE I

Amount of 0.1% reagent ml	*Optical density*
1	0.370
2	0.672
2.5	0.960
3.0	1.160
4.0	1.150
5.0	1.152
6.0	1.160

Effect of acidity. The effect of acid concentration on the absorbancy given by 40 γ zirconium is illustrated in Fig. 2. The optimum acidity is taken as 0.5N. The reagent absorbancy is independent of the pH. In view of the precipitation of zirconium as oxychloride in the higher pH range, only the absorbancy given by zirconium complex in acid medium has been studied. Hydrochloric acid is considered to be the best medium because of the greater stability of the zirconium complex.

Stability of the complex. No change in optical densities was noted for several hours after preparation of the zirconium-SPADNS solutions and thus, the system is sufficiently stable for quantitative determinations. Over a 4 week period under laboratory conditions of light and temperature, the optical density of 40 γ Zr in 25 ml volume remained almost unaltered.

References p. 66.

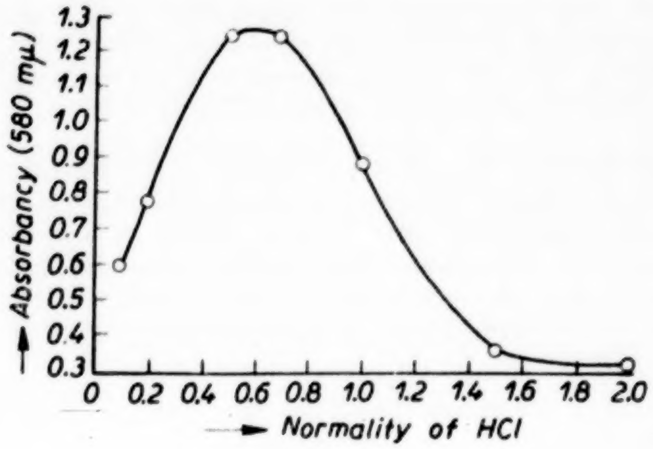

Fig. 2. Effect of acidity.

Adherence to Beer's law. Adherence to Beer's law in the concentration range, 7 to 56 γ ZrO_2 in 25 ml of final volume at 580 mμ is excellent, as shown by the data given in Table II and the calibration curve shown in Fig. 3.

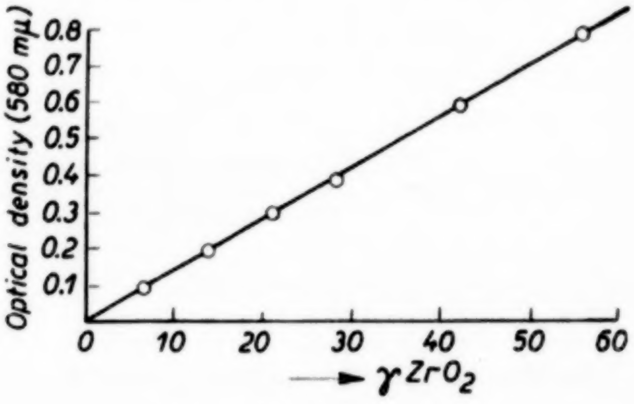

Fig. 3. Working curve.

TABLE II

3 ml of 0.1% reagent, 0.5N HCl, varying amounts of Zr in 25 ml volume *vs.* reagent

Zirconia present γ	*Optical density*
7	0.099
14	0.196
21	0.294
28	0.392
42	0.580
56	0.782

Sensitivity. The spectrophotometric sensitivity of the Zr-SPADNS colour system is either 0.075 γ Zr per cm^2 (practical) or 0.050 γ Zr per cm^2 (according to Sandell's definition).

Experimental procedure. Aliquots of 0.5, 1.0, 1.5, 2.0, 3.0 and 4.0 ml of zirconium standard which contained 14 γ of ZrO_2 per ml were pipetted into separate 25 ml volumetric flasks. To each flask were added 3 ml of 0.1% reagent and 0.5N HCl to make the volume 25 ml. Similarly, a reference solution was prepared by diluting 3 ml of 0.1% reagent to 25 ml with 0.5N HCl. The samples were then transferred to the 1 cm absorption cells and their optical densities were measured in the Unicam SP 600 spectrophotometer.

With a view to utilizing the reagent for the separation and co-determination of thorium and zirconium, the effect of acidity on the thorium-SPADNS complex has also been studied. 0.01N hydrochloric acid gives the best medium for the determination of thorium and with further increase in acidity, the thorium complex breaks down.

Composition of the coloured complex of zirconium

The empirical formula of the coloured complex of zirconium was determined as in the case of thorium (loc.cit.), except that 0.5*N* hydrochloric acid replaced 0.01*N* acid for the adjustment of pH. The slope ratio obtained in Fig. 4 is 1 : 1, thus, suggesting a 1 : 1 complex for zirconium with the reagent. The results are tabulated in Table III.

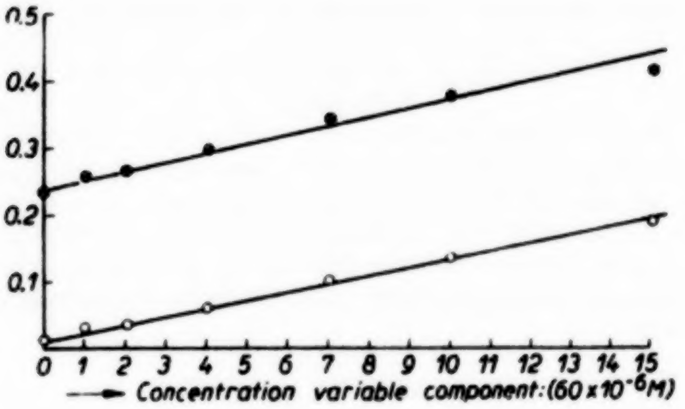

Fig. 4. Slope ratio: crimson-pink zirconium-SPADNS complex, pH 0.7, 580 mμ.
○ Reagent varying
● Zirconium varying
Constant component: $60 \cdot 10^{-5} M$.

TABLE III

SLOPE RATIO OF ZIRCONIUM COMPLEX

ml	*Optical density*
Zr($60 \cdot 10^{-5}M$) fixed : 10 ml, variable component: R($60 \cdot 10^{-6}M$)	
0	0.014
1	0.030
2	0.035
4	0.060
7	0.100
10	0.138
15	0.184
R($60 \cdot 10^{-5}M$) fixed: 10 ml, variable component: Zr($60 \cdot 10^{-6}M$)	
0	0.237
1	0.256
2	0.265
4	0.297
7	0.340
10	0.375
15	0.433

ACKNOWLEDGEMENTS

The author is indebted to Prof. P. RÂY for his kind advice and for providing all laboratory facilities. His thanks are also due to Mr. N. N. GHOSH of Science College, Calcutta for his valuable suggestions.

SUMMARY

A method has been developed for the spectrophotometric determination of microgram amounts of zirconium using SPADNS as the colour-forming agent. The method is sensitive and quantities as small as 0.07 γ of zirconium can be estimated in 25 ml of final volume. A standard calibration curve has been prepared; it conforms to Beer's law. The stoichiometric composition of the coloured complex has been determined spectrophotometrically by adopting the 'slope ratio method'.

RÉSUMÉ

Une méthode a été établie pour le dosage spectrophotométrique de quantités de zirconium de l'ordre du microgramme, au moyen de l'acide 2-(*p*-sulfophénylazo)-1,8-dihydroxynaphtalène-3,6-disulfonique (SPADNS). Cette méthode est sensible et des quantités allant jusqu'à 0.07 γ de zirconium peuvent être dosées dans un volume final de 25 ml. Une courbe d'étalonnage obéissant à la loi de Beer, a été tracée. La composition stoechiométrique du complexe coloré a été déterminée spectrophotométriquement.

ZUSAMMENFASSUNG

Eine empfindliche spektrophotometrische Methode zur Bestimmung von Zirkoniummengen von der Grössenordnung des Mikrogrammes mit Hilfe von 2-*p*-Sulfophenylazo-1,8-dihydroxynaphtalen-3,6-disulfonsäure (SPADNS) wird beschrieben. Es können Zirkoniummengen bis zu 0.07 γ in einem Volumen von 25 ml bestimmt werden. Eine Standardkalibrierkurve wurde gezeichnet; sie folgt dem Beer'schen Gesetze. Die stöchiometrische Zusammensetzung des gefärbten Komplexes wurde spektrophotometrisch ermittelt.

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SPECTROPHOTOMETRIC DETERMINATION OF SILICON IN THORIUM OXIDE*

by

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INTRODUCTION

The most commonly used spectrophotometric method for the determination of silicon is based on the absorbance of the colored molybdisilicic acid formed by the reaction of silicate with molybdic acid. Much of the early work was based on the absorbance of the yellow colored molybdisilicic acid. Later, the sensitivity of the method was improved by reducing the acid to a blue heteropoly form[1].

STRICKLAND[2], in his work on the preparation and properties of molybdisilicic acid found that there are two types, an α and a β form. The β complex, which is the more sensitive for spectrophotometric work, is usually formed by recommended analytical procedures[3]. In solutions having high concentrations of electrolyte, the molybdate species may be formed at the expense of the β-variety. Therefore, in analytical procedures, it is recommended that the total ionic strength of all the ions in the solution be restricted to about 0.5 and that the equivalents of hydrogen ion per gram ion of MoO_4^{-2} be about three to five[2].

In other spectrophotometric methods for the determination of silicon in thorium oxide, separation methods[4] have been utilized for removing either the thorium or the silicon prior to the determination. In the proposed method, the silicomolybdate complex is formed in the presence of thorium, thus avoiding the necessity of a preliminary separation of either the silicon or thorium. Under these conditions, a precipitate of thorium molybdate is obtained; however, when tartrate is added to the solution and the pH is raised to 3, this precipitate redissolves.

The development of this procedure also involved a study to establish the best conditions for the dissolution of the oxides of thorium and silicon. Factors which affect the color reaction such as reagent concentration, "salt" concentration, and effects of initial and final acidity were investigated. Finally, the precision and the accuracy of the method were evaluated.

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EXPERIMENTAL

Reagents

Ammonium molybdate solution (10% w/v). Dissolve 100 g of analytical reagent grade ammonium molybdate, $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$, in 1 liter of water.

1.2.4-*Aminonaphtholsulfonic acid solution*. Prepare solution A by dissolving 90 g of $NaHSO_3$ in 800 ml of water, and solution B by dissolving 7 g of Na_2SO_3 in 100 ml of water and adding 1.5 g of 1.2.4-aminonaphtholsulfonic acid. Mix solutions A and B thoroughly; then dilute to 1 liter. The solution is stable for about one month[5].

Ammonium hydroxide solution, silica free. Saturate water which is contained in a polyethylene bottle with ammonia gas.

Boric acid solution, saturated.

Hydrofluoric acid, analytical reagents grade, 48% HF.

Nitric acid, concentrated, density 1.41.

Standard solution of silicon, approximately 500 μg/ml. Dissolve 2.5 g of $Na_2SiO_3\cdot 9H_2O$ in 500 ml of water; then store in a polyethylene bottle. Standardize gravimetrically by the usual method based on dehydration with perchloric acid followed by ignition of SiO_2 and evaporation with HF to votatilize the silicon as SiF_4. Prepare more dilute solutions of silicon by making appropriate dilutions of the stock solution.

Tartaric acid solution (20% w/v). Dissolve 200 g of tartaric acid in 1 liter of water.

Water. Use distilled water in the preparation of reagents and in carrying out the procedure.

Spectrophotometer, Beckman, Model DU, with 5 cm cells.

pH Meter, Beckman, Model H2, or equivalent, equipped with glass and saturated calomel electrodes.

Platinum dishes, 100 ml.

Beakers, polyethylene, 250 ml.

Graduated cylinders, polyethylene, 100 ml.

Stirrer, mechanical, motor driven.

Procedure

Weigh 0.5 to 1 g of thorium oxide in a platinum dish. Add 5 ml of concentrated HNO_3, 25 ml of water, and one to two drops of 48 per cent HF[6]. For purposes of control, perform identical operations on all of the reagents throughout the procedure. Heat the mixture at approximately 80°C with occasional stirring until the thorium oxide dissolves. Keep the volume of the solution fairly constant by the occasional addition of water. When the solution becomes clear, allow it to cool; then transfer it to a graduated, 100 ml polyethylene cylinder that contains 30 ml of a saturated solution of boric acid. Dilute the solution to the 100 ml mark with water. Transfer an aliquot of the solution that contains from 2 to 40 μg of silicon to a 250 ml polyethylene beaker. Adjust the volume of the solution to about 50 ml with water. Add 15 ml of the ammonium molybdate reagent; then adjust the pH to within the range 0.9 to 1.4 by the addition of silica-free NH_4OH. Wait for 5 minutes; then add 20 ml of the tartaric acid solution. After about two minutes, add 1 ml of the 1.2.4-aminonaphtholsulfonic acid solution. Adjust the pH to 3.0 ± 0.1; then stir the solution until the precipitate of thorium molybdate dissolves. Transfer the solution to a 100 ml volumetric flask, dilute to volume with water; then mix thoroughly. Measure the absorbance of the solution *versus* water in 5 cm cells at a wavelength of 840 mμ. In the same manner, measure the absorbance of the reagent blank solution. Correct for the absorbance of the reagents by deducting the absorbance of the reagent solution from that of the sample.

Establish a calibration curve by transferring 20, 40, 80, and 160 μg of silicon to platinum dishes and repeating the steps in this procedure. A reagent blank is always carried through the entire procedure with each series of samples or standards.

The dissolution of thorium oxide

Thorium oxide must be dissolved by a procedure which will convert the silica quantitatively to soluble, reactive, silicate without loss of silicon. For most analytical purposes, thorium oxide is usually dissolved by boiling it in concentrated nitric acid to which a few drops of HF have been added. Since silicon can be volatilized from hot acidic solutions containing fluoride and since insoluble silica can be precipitated by dehydration in hot acidic solutions, it appeared probable that the conventional method for dissolving thorium oxide would not be satisfactory, when silicon was to be determined. Tests were, therefore, made which revealed that a portion of the silicon was lost if the sample was dissolved by boiling it in nitric acid containing some HF.

On still further examination, however, it was found that thorium oxide can be dissolved by heating it at 70 to 80°C in 4*M* nitric acid, which contained a small amount of HF. Although dissolution under these conditions requires a longer heating period as compared to dissolution in the concentrated acids no silicon was lost in this manner. Experimental results reveal that no silicon was lost during heating periods up to ninety minutes.

No difficulty was encountered in dissolving one-gram samples of thorium oxide by this method; dissolution was usually complete within 30 minutes. For larger samples, a more extended heating period and an additional drop or two of HF were required. The addition of fluoride, however, should be kept to a minimum. Accordingly, when too much fluoride had been added, thorium fluoride precipitated. When this occurs, the sample must be discarded and a smaller amount of HF added to a second portion of thorium oxide. The ratio of fluoride to thorium must be controlled rather closely to avoid precipitation of thorium fluoride.

The applicability of the method to the determination of silicon in thorium oxide was tested by recovering standard additions of silicon from a sample of thorium oxide which was essentially silica-free. This was accomplished by adding the silicon to weighed portions of the thorium oxide followed by the ignition of the test samples at 600°C for 30 minutes. This process converted the silicon to the insoluble form of SiO_2. The standard samples were then treated according to the recommended procedure. The results are shown in Table I.

TABLE I

THE ESTIMATION OF SILICON DIOXIDE AND THE EFFECT OF THORIUM OXIDE ON THE ABSORBANCE INDEX OF THE SILICOMOLYBDATE COMPLEX

Conditions:

Volume of test solution, ml	100
Aliquot for color development, ml	25
Final volume for color development, ml	100
pH	1.4
Final pH	3.0
Wavelength, mμ	840
Absorption cell, thickness, cm	5
Absorbance measured *versus* water and corrected for the reagent blank in all of the tests	

*Silicon**, *μg*	*Thorium oxide***, *g*	*Absorbance*	*Absorbance index* A_s
5	0.41	0.040	640
5	0.46	0.035	560
10	0.37	0.060	480
19	0.44	0.140	589
19	0.45	0.149	627
49	0.41	0.322	525
98	0.79	0.800	653
146	1.16	1.13	621
		Average	588
		Coefficient of Variation, *V*, per cent	10

* Silicon present in the initial test solution.

** Thorium oxide present in the initial test solution.

The average absorbance index of 615 which is calculated under these conditions agreed to within 1.5 per cent with the absorbancy index of 622 which is shown in Table II. This constancy in the absorbance index indicates that the presence of varying amounts of thorium does not affect the color reaction and that the insoluble silicon in the form of SiO_2 is converted to the soluble reactive fluorsilicate by the nitric acid and hydrofluoric acid treatment recommended herein.

Effect of nitrate ion

It was previously reported[2,5] that full development of the color of the silicomolybdate complex is not attained in solutions of high ionic strength. In view of this and the concomitant fact that a considerable amount of nitric acid must be neutralized to a pH of 1.4 prior to the development of the color, it became necessary to evaluate the effect of varying concentrations of ammonium nitrate upon the absorbance. As a consequence of this study, it was found out that when the color was developed in solutions at a pH of 1.4 the absorbance was independent of the ammonium nitrate concentration over the range from 0.3 to 1.2*M*. In the absence of nitrate, however, as is shown in Fig. 1, the absorbance was appreciably decreased.

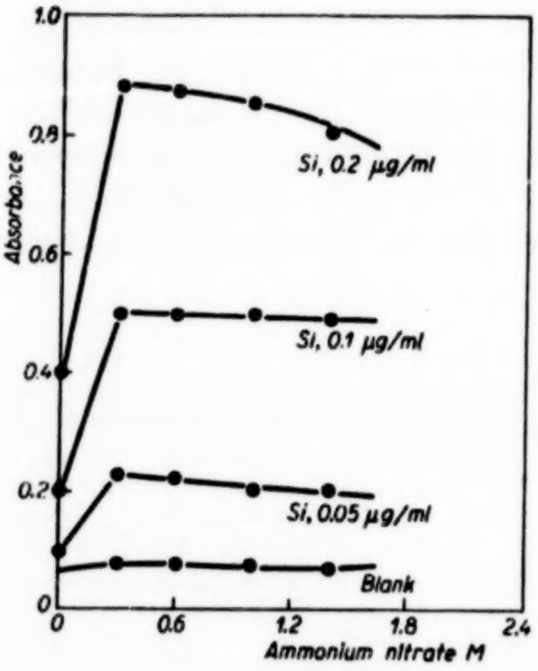

Fig. 1. The effect of ammonium nitrate on the color intensity of the silicomolybdate complex.

Conditions:

Initial pH	1.4
Final pH	3.0
Wavelength	840 mµ
Cell path	5 cm

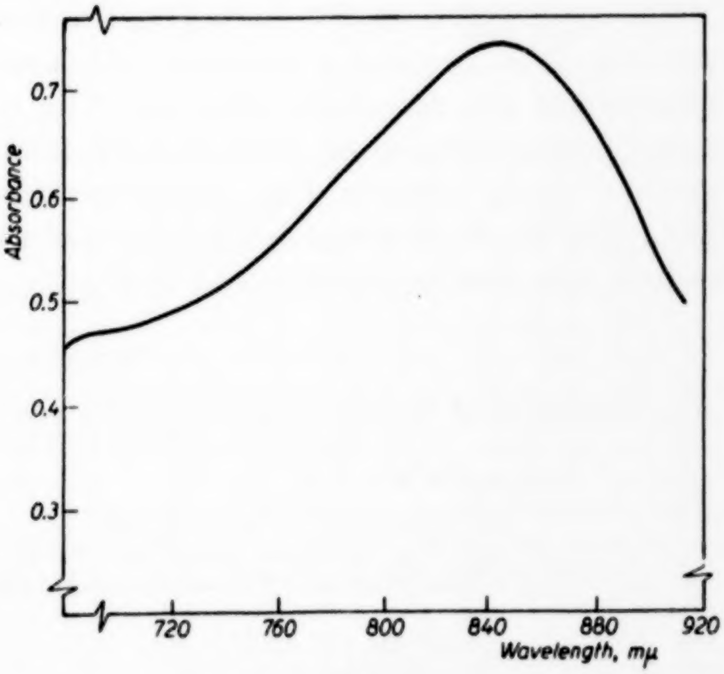

Fig. 2. The absorbance maximum of the blue silicomolybdate complex.

Conditions:

Silicon	1 µg/ml
Cell path	1 cm
Absorbance *vs.* H_2O	
Initial pH	1.4
Final pH	3.0

To secure best results, the acidity of the test solutions prior to the adjustment of the pH to 1.4 was maintained in the concentration range from 0.3 to 1*M*. For this reason and the fact that 4*M* nitric acid was required to disolve the samples of thorium oxide, aliquots of the solution were taken for the development of color instead of the entire volume.

Dissolution of thorium molybdate

Another problem that was associated with the formation of the silicomolybdate complex in the presence of large amounts of thorium was the difficulty of achieving complete solution of the thorium molybdate. In order to redissolve the thorium molybdate after the addition of the tartaric acid, the pH had to be adjusted to 3.0 when as much as 500 mg of thorium was present, the dissolution was facilitated greatly by transferring the mixture to a 100 ml volumetric flask after adjusting the pH to 3.0 and swirling the flask under a hot water tap for a few minutes.

Wavelength of maximum absorbance

The absorbance of the blue silicomolybdate complex was found to be a maximum at a wavelength of 840 mμ both in the presence or absence of thorium. The absorption spectrum is shown in Fig. 2.

CARLSON AND BANKS[5] reported that maximum absorbance occurred at a wavelength of 815 mμ. These measurements were however, made at a pH of 1.2 whereas, in the present work, measurements are made at a pH of 3.0. This difference in pH at which measurements of absorbance are made may be responsible in part, at least, for the shift of absorbance maximum to a higher wavelength, namely, 840 mμ.

Determination of the absorbance index

A calibration index was established for the determination of silicon by treating known amounts of silicon according to the procedure recommended in this report.

The absorbance index of silicon in the form of the blue silicomolybdate complex was calculated from the following relationship:

$$A_s = \frac{A}{Cb}$$

Where A_s = absorbance index
A = absorbance
C = concentration = g per 1000 g of solution
b = thickness of absorbance cells, cm

The results are presented in Table II. The data represent the averages of determinations that were carried out over a period of several weeks.

It is indicated from the data that the absorbance index that was obtained from different determinations over a period of several weeks is reproducible to about 5 per cent and that Beer's law is obeyed over the concentration range that was studied.

Factors affecting the color intensity of the blue silicomolybdate complex

In the development of this procedure, the following factors which might affect the color intensity were investigated.

Effect of initial pH

Formation of the molybdisilicic acid was investigated at initial pH values other than 1.4. It was found that the color intensity of the final silicomolybdate complex remains unaltered if the molybdisilicic acid is formed in solutions, the pH of which ranges from 0.9 to 1.5. This is in agreement with previous findings[5]. When, however, the complex was formed at a pH of 5, six-fold decrease in absorbance was noted.

TABLE II

REPRODUCIBILITY OF THE ABSORBANCE INDEX FOR SILICON

Conditions:

Volume of test solution, ml	100
Aliquot for color development, ml	20
Final volume for color development, ml	100
pH	1.4
Final pH	3.0
Wavelength, mμ	840
Absorption cell, cm	5
Absorbance measured *versus* water, corrected for the reagent blank	

Silicon, μg*	*Determinations, n*	*Average absorbance, A*	*Absorbance index, A_s*	*Coefficient of variation*
25	4	0.150	600	8
50	5	0.290	580	5
100	5	0.650	650	3
145	5	0.940	648	4
		Average	619	5

* Silicon present in the initial test solution.

Effect of final pH

Since a pH of 3.0 is mandatory for the dissolution of thorium molybdate, the effect of elevating the final pH to 3.0 on the color intensity of the blue complex was investigated. The results, represented in Fig. 3, show that the absorbance of the silicomolybdate complex is not appreciably affected when the pH is elevated to a final value of 3.0. A slight decrease in absorbance was evident, however, when the pH was increased to 3.5, while, above a pH of 3.5, the absorbance decreases rapidly; therefore, in all of the tests, the final pH was maintained at 3.0.

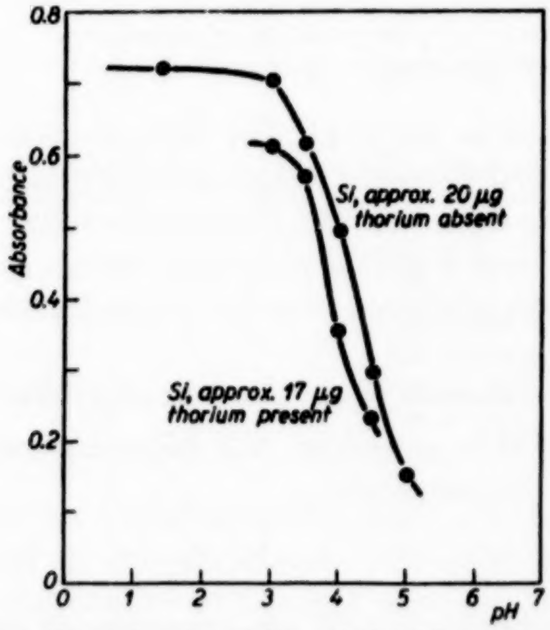

Fig. 3. The effect of pH on the color intensity of the blue silicomolybdate complex.

Conditions:

Initial pH	1.4
Wavelength	840 mμ
Cell path	5 cm
Final volume	100 ml

References p. 75.

Concentration of molybdic acid

Since thorium is precipitated as thorium molybdate on the addition of ammonium molybdate, it was necessary to determine the volume of reagent which is required for the complete development of the molybdisilicic acid. In the presence of 100 to 200 mg of thorium, 15 ml of the ammonium molybdate reagent was found to be sufficient for full color development of the silicomolybdate complex. This provides a molybdate concentration of approximately $0.1 M$ after the thorium is precipitated. Low recoveries of silicon were obtained when less than 15 ml were used for the formation of molybdisilicic acid in the presence of thorium. Large excesses of molybdate are to be avoided, however, because of the possibility of reducing some of the molybdate, in addition to the silicomolybdate complex, to molybdenum blue[5].

Effect of time between the addition of tartrate and the reducing agent

In the absence of phosphate, the addition of tartrate can be made after the reduction of the silicomolybdate complex to the heteropoly blue form. Under these conditions, it was found that the time interval before the measurement of the absorbance of the solutions does not have to be considered. If phosphate is present, the tartaric acid is added first. It was previously established[7] that the addition of tartaric acid prior to reduction disassociated the phosphomolybdate complex and therefore eliminated any interference due to its presence. Since tartaric acid may also disassociate the molybdisilicic acid to some extent, it was necessary to determine the criticality of the time interval between the addition of the two reagents. The time interval between the addition of tartaric and sulfonic acids was varied from 0 to 20 minutes. No change was observed in the absorbance measurements for periods up to 5 minutes. A gradual decrease in absorbance was evident, however, for the period from 5 to 20 minutes. The same effect was noted in those solutions which contained thorium. It was concluded, therefore, that, in the presence of phosphate, a time interval up to five minutes is not critical for securing reproducible measurements of the absorbance, but that the absorbance must be measured within 5 minutes of the time the reduction is carried out.

The reagent blank

When reagent blank solutions were processed in glass-ware, the absorbance was abnormally high due to silicon contamination, even though boric acid had been added to mask the fluoride ions. The contamination was less pronounced with sample solutions containing large amounts of thorium. In order to eliminate this source of error, all dilutions prior to the formation of the blue silicomolybdate complex were made in polyethylene containers.

Even though the use of polyethylene containers decreased the absorbance of the reagent blank solution appreciably, the absorbance was still rather high and variable (0.070 to 0.120), due to traces of silicon in the reagents, particularly in the hydrofluoric acid. Consequently ,the absorbance of the reagent blank solution was measured *versus* water and deducted from the absorbance of the sample solution also measured *versus* water, rather than measure the absorbance of the sample *versus* the reagent solution. Thus, the operator was made aware of the magnitude of the reagent blank absorbance so that corrective measures could be taken, should the absorbance of the reagent blank be abnormally large.

References p. 75.

Estimation of precision from duplicate tests

The precision of the method, when applied to the analysis of silicon in samples of thorium oxide from different sources, was calculated from the difference between duplicates[8].

The silicon content of the samples varied from 20 to 200 p.p.m. In general, good agreement was obtained between duplicates. The coefficient of variation which was calculated for eleven samples was of the order of 13 per cent. This error, when compared to the coefficient of variation of the standard curve alone, which was 5 per cent, indicates that the method appears to have a larger error when applied to the actual analysis of samples. In part this may be due to errors in sampling.

Interferences

Phosphate when present in amounts up to a total of 400 micrograms does not interfere when tartrate is used to disassociate the phosphomolybdate complex. The tartrate is added to the solution prior to the reduction of the silicomolybdate complex to the heteropoly blue form.

Large quantities of iron(II) interfere because of a reaction with the molybdic acid; whereas, iron(III) interferes because it consumes some of the reducing agent[5]. It is necessary, therefore, to separate the iron prior to the determination of silicon.

High concentrations of electrolyte, such as halides, nitrates and sulfates prevent maximum development of the color and are to be avoided[5].

CONCLUSION

The proposed method for the determination of silicon compares favorably with other spectrophotometric procedures that have been developed. This method is applicable to the determination of silicon in the presence of thorium; whereas, in earlier publications it is recommended that the silicon be separated from thorium prior to the estimation of silicon.

Phosphate up to a total of 400 micrograms does not interfere. Large quantities of iron(II) interfere by direct reaction with molybdic acid; whereas, iron(III) interferes by consuming the reducing agent[5]. High concentrations of halides, nitrates and sulfate prevent maximum color development and are to be avoided.

ACKNOWLEDGEMENTS

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SUMMARY

A method is described for the spectrophotometric determination of microgram quantities of silicon in the presence of thorium. Thorium oxide is dissolved by heating it at 70 to 80°C in $4M$ HNO_3 that contains 2 drops of HF. Under these conditions, no silicon is lost through volatilization. The silicon is estimated as the blue silicomolybdate complex. Under the conditions selected for development of color, a precipitate of thorium molybdate is obtained; the thorium molybdate is, however, dissolved without affecting the color of the complex by the addition of tartrate and adjusting the pH of the solution to 3.0. The lower limit of detection is about 5 p.p.m. of silicon.

References p. 75.

RÉSUMÉ

Une méthode est décrite pour le dosage spectrophotométrique de quantités de silicium de l'ordre du microgramme en présence de thorium. L'oxyde de thorium est dissous à 70-80°C dans l'acide nitrique 4*M*, contenant deux gouttes d'acide fluorhydrique. Dans ces conditions on n'observe aucune perte de silicium par volatilisation. Le silicium est finalement dosé sous forme du silicomolybdate complexe bleu. Dans les conditions adoptées pour l'obtention de la coloration bleue, le molybdate de thorium précipite; on peut cependant le redissoudre par addition de tartrate et en portant le pH à 3.0, sans altérer la coloration de la solution. La limite inférieure de détection du silicium est d'environ 5 p.p.m.

ZUSAMMENFASSUNG

Eine Methode zur spektrophotometrischen Bestimmung des Siliciums in Mikrogramm-Mengen in Gegenwart von Thorium wird beschrieben. Das Thoriumoxyd wird durch Erhitzen auf 70-80°C in 4*M* Salpetersäure, die 2 Tropfen HF enthält, gelöst. Unter diesen Bedingungen wurde kein Siliciumverlust durch Verflüchtigung beobachtet. Das Silicium wird als blauer Siliciummolybdat-Komplex bestimmt; unter den für die Entwicklung der Farbe gewählten Bedingungen, entsteht auch ein Thoriummolybdat-Niederschlag, welcher aber durch Zugabe von Tartrat und durch Einstellung des pH auf 3.0 in Lösung gebracht werden kann, ohne dass die Farbe des Komplexes hierdurch beeinflusst wird. Die untere Erfassungsgrenze ist ungefähr 5 Teile pro Million.

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MICRO-HETEROMETRIC DETERMINATION OF MOLYBDIC ACID WITH α-BENZOIN OXIME

by

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INTRODUCTION

Studies using the heterometric method have been presented in many previous papers[1]. The fundamentals of heterometry have also been discussed briefly in a special report[2].

α-Benzoin oxime (α-BO) in ammoniacal solution precipitates many cations, especially copper, which is precipitated even from ammoniacal tartrate solution[3]. Several metals, which if present in acid form such as molybdic or tungstic acid, are precipitated from strongly acidic solution. These are soluble in ammoniacal solution.

The separation of metals from one another is therefore possible by working either in acid or alkaline solution. The following experiments show that small amounts of molybdic acid can be determined heterometrically with satisfactory results in the presence of large excesses of almost all other metals without previously separating. The foreign metals mostly made up 99 to 99.8% of the total metal content. The titrations lasted about half an hour at room temperature and the error was generally between 0.0 and 1.6%. The following foreign ions were present in excesses: Ca^{+2}, Ba^{+2}, Mg^{+2}, Zn^{+2}, Mn^{+2}, Co^{+2}, Ni^{+2}, Fe^{+3}, Al^{+3}, Cr^{+3}, Cd^{+2}, Cu^{+2}, Pb^{+2} and UO_2^{+2}. In addition, the solution could contain excesses of tungstic and vanadic acids. As the maximum density values obtained in the presence of most of the above cations were hardly different from those obtained in their absence, it is almost certain that the foreign salts concerned may be present in a much higher concentration without affecting the results.

EXPERIMENTAL

The instrumentation and the working conditions were the same as in previous investigations[1]. The chemicals were all either analytical reagents or chemically pure reagents. The $Na_2MoO_4 \cdot 2H_2O$ was a May & Baker c.p. reagent and the *α*-benzoin oxime was a c.p. Amend Drug reagent. The latter was dissolved in ordinary pure alcohol.

The precipitate obtained was white and the solution was colourless. Therefore, no coloured filter was used. It was found that in some cases the use of a blue filter produced higher maximum density values. In other cases practically the same results were obtained without a filter as with a blue filter, but in no case was the density lower with the blue filter. In order to clarify the situation, some parallel experiments were carried out with and without the filter. In many other cases, the titrations were only carried out with a blue filter. (The experiments in which a blue filter was used are designed in the Table with a + .)

RESULTS

Table I and Fig. 1 give the composition and results of a selection of the heterometric titrations made. Fig. 2 presents the course of selected titrations. The same numeration is used in Table I and Fig. 2.

pH-Heterometric study

Fig. 1 presents the results of parallel pH and heterometric titrations which were carried out in two ways, either beginning with solutions at a high pH and gradually decreasing the pH by the addition of acid, or, *vice versa*, titrating suspensions formed at low pH's by the addition of alkali. These titrations lasted longer than usual because measurements were only made after stable density values had been reached.

Analysing the curve of Fig. 1 the following conclusions were arrived at. At high pH's the molybdic acid-oximate compound does not exist (curves 1 and 2). On decreasing the pH, the precipitation of the insoluble molybdic oximate compound begins at approximately pH 5.6. The precipitation mainly occurs in the pH region between 4.5 and 2.7. At pH 2.7 the precipitation is complete and increased acidity appears to have no further influence. pH 2.7 is probably the highest pH at which quantitative precipitation of the oximate occurs.

Another picture is obtained by analysing the results of curves 3 and 4 which show the *dissolution* of a precipitate obtained at a low pH. In this case, on increasing the pH, the suspension begins to dissolve at pH 8.0 and a clear solution is only obtained at pH>11. The apparent contradiction in the results can be explained in this case,

TABLE I

Composition: 5 ml 0.0025*M* Na_2MoO_4 + *a* ml supplements + (15-*a*) ml H_2O + *x* ml 0.01*M* benzoin oxime (BO).
Content: 1.2 mg Mo. Temp. = 20°C. Concentration: $6.3 \cdot 10^{-4}$*M*.

Expt. no.	*Supplements*	*% Mo*	*ml BO found [x]*	*Initial precipitation at ml*	*Maximum density value*	*Approximate titration time in min*	*Blue filter*	*% error*
1	H_2O			∞	0.0			
2	1 ml *M* HNO_3		*c* 3.10	0.2	0.37	30	—	0.0
3	1 ,, ,, ,,		*c* 3.10	0.6	0.38	30	+	0.0
4	3 ,, ,, ,,		*i* 3.06	0.4	0.29	30	—	1.3
5	3 ,, ,, ,,		*i* 3.02	0.6	0.33	30	+	2.4
6	1 ,, ,, ,, + 5 ml *M* NH_4NO_3		*i* 3.10	0.4	0.32	25	—	0.0
7	1 ,, ,, HCl		*c* 3.05	0.4	0.32	32	—	1.6
8	1 ,, ,, ,,		*c* 3.05	0.6	0.39	30	+	1.6
9	3 ,, ,, ,,		*i* 3.10	0.4	0.28	26	—	0.0
10	3 ,, ,, ,,		*c* 3.05	0.6	0.35	30	+	1.6
11	3 ,, ,, H_3PO_4		∼ 3.14	0.6	>0.37	32	—	1.3
12	2 ,, ,, HCl + 5 ml 0.1*M* Na_2WO_4	1.2	*c* 3.05	0.4	0.32	28	+	1.6
13	1 ,, ,, ,, + 1 ,, ,, ,, $NaVO_3$	29.0	*i* 3.10	0.6	0.39	100	—	0.0
14	1 ,, ,, ,, + 5 ,, *M* $Ca(NO_3)_2$	0.6	3.07	0.6	0.30	35	—	1.0
15	1 ,, ,, ,, + 5 ,, ,, ,,	0.6	*c* 3.08	0.4	0.42	32	+	0.6
16	1 ,, ,, ,, + 5 ,, ,, $BaCl_2$	0.2	3.05	0.8	0.29	35	—	1.7
17	1 ,, ,, ,, + 5 ,, ,, ,,	0.2	*c*∼ 3.10	0.6	0.35	32	+	0.0
18	1 ,, ,, ,, + 5 ,, ,, $MgCl_2$	1.0	*i* 3.0	0.4	0.36	27	—	3.0
19	1 ,, ,, ,, + 5 ,, ,, ,,	1.0	3.0	0.6	0.40	32	+	3.0
20	1 ,, ,, ,, + 5 ,, ,, $MgNO_3$	1.0	3.05	0.2	0.33	32	—	1.7
21	1 ,, ,, ,, + 5 ,, ,, ,,	1.0	*i* 3.10	0.6	0.47	30	+	0.0
22	1 ,, ,, ,, + 5 ,, ,, $ZnSO_4$	0.4	*i* 3.10	0.6	0.36	31	—	0.0
23	1 ,, ,, ,, + 5 ,, ,, ,,		*c* 3.15	0.6	0.44	30	+	1.6
24	1 ,, ,, ,, + 5 ,, ,, $MnCl_2$	0.4	*i* 3.10	0.6	0.45	30	+	0.0
25	1 ,, ,, ,, + 5 ,, ,, $NiCl_2$	0.4	*i* 3.06	0.6	0.28	34	—	1.3
26	1 ,, ,, ,, + 1 ,, ,, $Co(NO_3)_2$	2.0	*i* 3.10	0.6	0.25	22	—	0.0
27	1 ,, ,, ,, + 1 ,, ,, ,,		*c* 3.0	0.4	0.36	35	+	3.0
28	1 ,, ,, ,, + 5 ,, ,, ,,	0.4	*i* 3.05	0.6	0.27	32	+	1.6
29	1 ,, ,, ,, + 1 ,, ,, (UO_2) $(NO_3)_2$	0.5	3.10	0.2	0.51	105	—	0.0
30	1 ,, ,, ,, + 5 ml *M* $AlCl_3$	0.9	*i* 3.13	0.6	0.43	27	+	1.0
31	1 ,, ,, ,, + 5 ,, ,, ,,		*i* 3.10	0.6	0.40	32	—	0.0
32	1 ,, ,, ,, + 1.5 ,, ,, 2*M* Fe $(NO_3)_3$	0.7	*i* 3.12	0.6	>0.40	40	—	0.6
33	1 ,, ,, ,, + 1.5 ,, ,, ,, ,,		*i* 3.1	0.8	0.41	42	+	0.0
34	3 ,, ,, ,, + 1 ml *M* $Fe(NO_3)_3$ + 3ml *M* Na_3-citrate	2.1		∞	0.0			
35	1 ,, ,, ,, + 1 ,, ,, $Cr(NO_3)_3$	2.2	3.05	0.4	0.20	26	—	1.6
36	3 ,, ,, ,, + 1 ,, ,, K_2CrO_4	2.2	*i* 3.2	0.4	>0.42	80	—	3.2
37	1 ,, ,, ,, + 5 ,, ,, $Cd(NO_3)_2$	0.3	3.06	0.4	0.51	27	+	1.3
38	1 ,, ,, ,, + 5 ,, ,, ,,	0.3	3.10	0.6	0.26	35	—	0.0
39	1 ,, ,, ,, + 5 ,, ,, $Cu(NO_3)_2$	0.4	*i* 3.10	0.6	0.39	35	—	0.0
40	1 ,, ,, HNO_3 + 5 ,, ,, ,,		3.10	0.8	0.34	27	—	0.0
41	1 ,, ,, ,, + 5 ,, 2*M* $MgCl_2$ + 1 ml 0.1*M* $Pb(NO_3)_2$	5.5	*i* 3.06	0.6	0.46	95	+	1.3

c = contact point; *i* = intersection

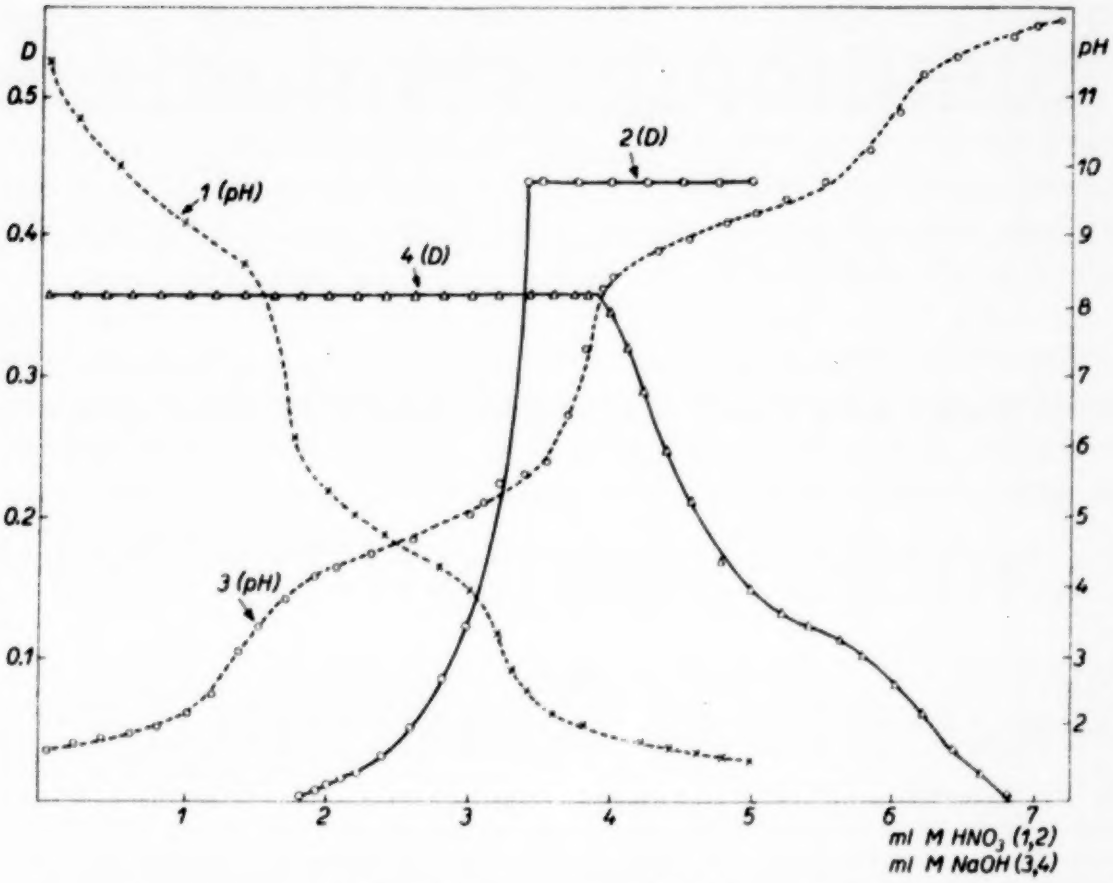

Fig. 1. Curves 1 and 2: 5 ml 0.0025*M* Na_2MoO_4 + 4 ml 0.01 *M* α-benzoin oxime + 2 ml *M* NH_4NO_3 + 2 ml *M* Na acetate + 2.5 ml *M* NaOH + 4.5 ml H_2O + *x* ml *M* HNO_3.
Curves 3 and 4: 5 ml 0.0025 *M* Na_2MoO_4 + 4 ml 0.01 *M* α-benzoin oxime + 2 ml *M* NH_4NO_3 + 2 ml *M* Na acetate + 3 ml *M* HNO_3 + 4 ml H_2O + *x* ml *M* NaOH.

as in similar cases, by the transformation in the physical state which the solid particles undergo in experiments 3 and 4. These particles which already exist in the suspension and which are to be dissolved by the addition of alkali, are not easily susceptible to attack by the alkali. Therefore, the results of curves 1 and 2 which were obtained by the *formation* of the insoluble compound, and which are not influenced by the character of the solid produced, give a true picture of the pH concerned in the precipitation.

Composition of the compound precipitated

In all titrations carried out in acid solution by the dropwise addition of α-BO to the molybdic acid, the first maximum density point was obtained at the molar ratio of 2.5 α-BO : 1 molybdic acid ($((MoO_3)_2\ (\alpha\text{-}BO)_5)$).

Titrations in the absence of foreign metals

Although the maximum density values obtained with the amount of molybdate cited, were relatively low, they were entirely sufficient to ensure a safe determination of the end-point. There appears to be no difference in the results whether nitric or hydrochloric (or even phosphoric) acid were used.

Table I, expts. 1-10, shows the results of titrations which were mostly carried out in the presence of strong mineral acids. There appears to be no difference between the results obtained without or with a filter.

References p. 80.

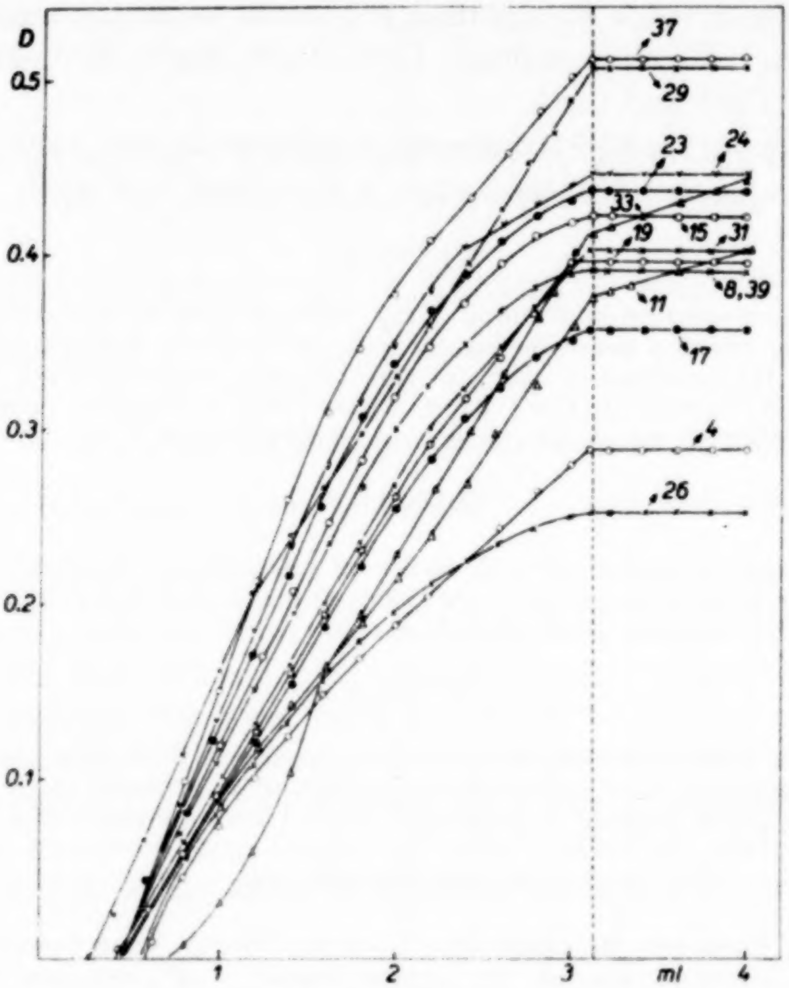

Fig. 2. Titrations of sodium molybdate with α-benzoin oxime.

Titrations in the presence of excesses of foreign metals

In no case were complexing agents used. The amount of *lead* was greatly restricted (expt. 41) as otherwise a precipitation formed before the titration. Also the maximum density line obtained showed fluctuations. It was found that this could be avoided by the addition of large excesses of chloride as magnesium chloride to the titrated solution. In the case of *vanadic acid* (expt. 13) the titration lasted much longer than usual although the molybdenum made up 29%. Wolframate could be present up to 99% (expt. 12). There was no difference whether the salts were present as sulfate, chloride or nitrate. Generally, an increase in the concentration of the foreign cation added, hardly influenced the maximum density value. Therefore, it is almost certain that the amount of foreign metal may be further increased without harming the determination. Only in the case of *chromium (III)* (because of the intensity of the colour) was the amount present somewhat restricted and the molybdenum made up 2.2% of the total (expt. 35). In the presence of larger amounts of *ferric iron* no horizontal maximum density line was obtained: the density value rose linearly after the calculated end-point but in another direction. In this case the end-point was obtained by the intersection of the maximum line with the last part of the titration line. An attempt was made to reduce the ferric iron before the beginning of the titration by the addition of an acid solution of sodium sulfite but the results were even less satisfactory than the straight titration in the presence of ferric iron. In the presence of *uranyl nitrate* (expt. 29) the result is satisfactory but the titration time is very extended.

Molybdic acid, which made up less than 1%, could be satisfactorily determined in the presence of the following cations: Ca^{+2}, Ba^{+2}, Mg^{+2}, Zn^{+2}, Mn^{+2}, Co^{+2}, Ni^{+2}, UO_2^{+2}, Al^{+3}, Fe^{+3}, Cd^{+2} and Cu^{+2}.

A large amount of Co^{+2} or Ni^{+2} reduces the maximum density value. With cadmium a higher density value was obtained when a blue filter was used.

METHOD

20 ml of an aqueous solution containing 1 mg molybdenum as molybdic acid and 1-3 ml M HCl or HNO_3, are titrated heterometrically with an alcoholic solution of 0.01 M α-benzoin oxime. The solution may contain ∿ 99% of the following cations: Ca^{+2}, Ba^{+2}, Mg^{+2}, Zn^{+2}, Mn^{+2}, Co^{+2}, Ni^{+2}, Fe^{+3}, Cr^{+3}, Al^{+3}, Cd^{+2}, Cu^{+2}, Pb^{+2}, $(UO_2)^{+2}$, tungstic or vanadic acids. The titration lasts about half an hour and the error is generally 0-2%.

SUMMARY

1 mg of molybdenum as molybdic acid in 20 ml solution can be titrated heterometrically with α-benzoin oxime in the presence of ∿ 99% of most bivalent or trivalent cations as well as in excesses of tungstic or vanadic acids. Error: 0-2%.

RÉSUMÉ

1 mg de molybdène sous forme d'acide molybdique peut être dosé dans une solution de 20 ml par la méthode hétérométrique à l'aide de l'α-benzoïnoxime en présence de ∿ 99% de la plupart des cations bi- ou trivalents, ainsi qu'en présence d'excès d'acide tungstique ou d'acide vanadique. Erreur: 0-2%.

ZUSAMMENFASSUNG

1 mg Molybdän in Form von Molybdänsäure in 20 ml Lösung, kann heterometrisch mit Hilfe von α-Benzoinoxim bestimmt werden. Die Lösung kann ∿ 99% von den meisten zwei- oder dreiwertigen Kationen, sowie Überschüsse von Wolfram- oder Vanadinsäure enthalten. Fehler: 0-2%.

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QUINQUEVALENT TUNGSTEN AS A REDUCING AGENT IN POTENTIOMETRIC TITRATIONS

II. ESTIMATION OF CERIC SALTS, BROMATE AND FERRICYANIDE

by

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In previous investigations, quinquevalent tungsten was applied to the reductimetric estimation of dichromate, ferric iron, iodate, cupric copper[1] and quinquevalent vanadium[2]. The reagent was also found successful for the microdetermination of quinquevalent vanadium[2], dichromate, ferric iron and bivalent copper[3]. The latter two could be further titrated simultaneously in a mixture containing them. In this investigation we extended our study to other oxidants including ferricyanide bromate and ceric salts either alone or in admixture with ferric iron, dichromate or vanadate.

EXPERIMENTAL

The titration device and experimental technique are the same as previously described[1]. The titrations are carried out in an atmosphere of carbon dioxide.

Solutions

Quinquevalent tungsten was prepared by the electrolytic reduction of sodium tungstate in 10*N* HCl[1]. Solutions of oxidants to be titrated, *viz.* ceric and ferric salts, ferricyanide, dichromate, bromate and vanadate, were prepared from the C.P. and AnalaR products. They were standardized by the use of recommended procedures[4].

RESULTS AND DISCUSSION

A. Titration of ceric solutions

Owing to the high redox potential of the Ce^{+4}/Ce^{+3} system which amounts to 1.6 volts[5], successful titrations could be performed in the presence of HCl only at low acid concentrations. But, under these conditions, tungstic acid is liable to separate out rendering the reaction sluggish and the results inaccurate. Although the separation of tungstic acid could be overcome in the cases previously studied by adding H_3PO_4[1], yet in the case of ceric solutions, the reaction medium becomes turbid and the reaction very slow. Thus in this latter case the equilibrium was attained within 10-20 min after each addition of 0.1 ml of titrant. Although the titration could not be recommended for the analysis of ceric salts, nevertheless more or less good results were obtained, indicating that the reaction is quantitative. Calculation of the equilibrium constant and the degree of completion of the reaction, using the formal redox potentials of the

Ce^{+4}/Ce^{+3} and the W^{+6}/W^{+5} systems as evaluated from the experimental results[1] (*cf.* Fig. 1, curves A and B), yield values of $6.3 \cdot 10^{-34}$ and $2.46 \cdot 10^{-17}$ respectively.

Recourse was therefore taken to the reverse process of titrating quinquevalent tungsten with ceric solutions. This process is more advantageous because the titrations can be done in the presence of concentrated HCl ($\sim 7N$) without loss of chlorine by oxidation. Under these conditions the solution remains clear and the reaction takes place rapidly at the beginning, but slows near the end-point when it needs ~ 5 min for the attainment of equilibrium. The results are more or less quantitative when

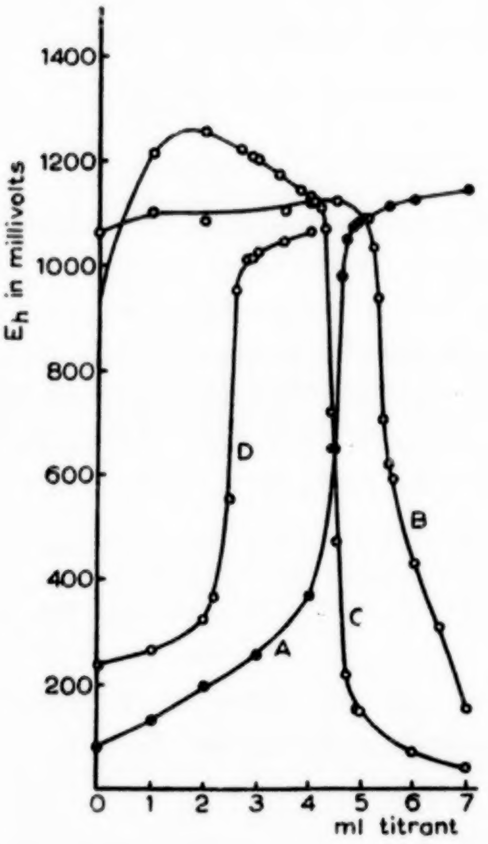

Fig. 1.

A. 10 ml $0.00393N$ W^{+5} in $7N$ HCl + $0.5N$ H_3PO_4 titrated with $0.0086N$ Ce^{+4}.
B. 5 ml $0.0086N$ Ce^{+4} in $0.5N$ H_3PO_4 titrated with $0.00796N$ W^{+5} (in $10N$ HCl).
C. 5 ml $0.01N$ $KBrO_3$ in $0.5N$ H_3PO_4 titrated with $0.01136N$ W^{+5} (in $10N$ HCl).
D. 5 ml $0.00510N$ W^{+5} in $10N$ HCl titrated with $0.01N$ $KBrO_3$.

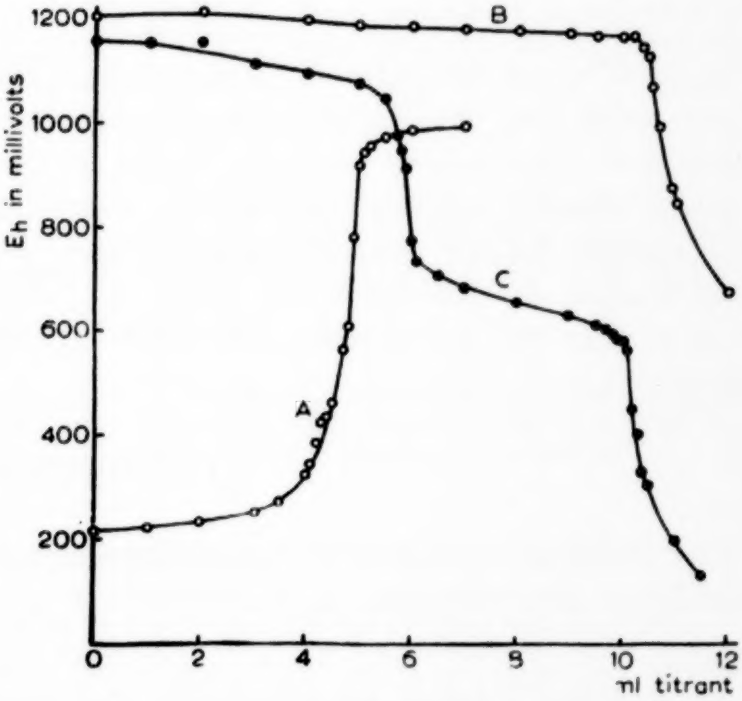

Fig. 2.

A. 10 ml $0.00437N$ W^{+5} in $10N$ HCl titrated with $0.00893N$ $K_3[Fe(CN)_3]$.
B. 5 ml $0.01418N$ $K_3[Fe(CN)_6]$, in presence of $0.5N$ H_3PO_4 titrated with $0.00675N$ W^{+5} (in $10N$ HCl)
C. 2.5 ml $0.01418N$ $K_3[Fe(CN)_6]$ + 2.5 ml $0.00991N$ Fe^{+3} in $0.5N$ HCl + $0.5N$ H_3PO_4 titrated with $0.0059N$ W^{+5} (in $10N$ HCl).

TABLE I

OXIDATION OF W^{+5} WITH $0.0086N$ Ce^{+4}

Acidity	*Normality of W^{+5}*	*Max. inflection per 0.1 ml mV*	*Theor. end-point ml*	*Exptl. end-point ml*	*Error %*
$10N$ HCl	0.00410	141	4.77	4.76	—0.21
$8N$ HCl	0.00386	170	4.49	4.48	—0.22
$7.5N$ HCl	0.00404	256	4.70	4.72	0.43
$7N$ HCl	0.00402	261	4.67	4.68	0.21
$7N$ HCl + $0.5N$ H_3PO_4	0.00393	106	4.57	4.57	0.0
$8N$ H_3PO_4	0.00394	299	4.58	4.58	0.0

done at acidities higher than $7N$. If the acidity falls below $6N$ the solution gets turbid and the results become inaccurate. Curve A, Fig. 1, represents the titration of W^{+5} in $0.5N$ H_3PO_4 + $7N$ HCl with Ce^{+4}, whereas curve B shows the reduction of Ce^{+4} in $10N$ HCl.

B. Titration of potassium bromate solution

Quinquevalent tungsten reduces bromate solutions rapidly at room temperature, but the titrations could not be done in the presence of high HCl concentrations owing to the evolution of chlorine. Contrary to the case of ceric solutions it is possible to carry out the reactions at low acidities in the presence of phosphoric acid. Under these latter conditions good results could be obtained. The reaction is rapid at the beginning of the titration but slows somewhat at the end-point (curve C, Fig. 1).

On titrating quinquevalent tungsten with bromate on the other hand, the same phenomena as observed with ceric salts are met with. The reaction occurs rapidly even at room temperature and can be performed at high acid concentrations without the loss of oxidant through interaction with hydrochloric acid. In both cases, *viz.* the direct reduction of ceric solution and the reverse titration, the results are quantitative. The degree of completion as calculated from the formal redox potentials amounts to $3.10 \cdot 10^{-14}$. The titration curves are more or less smooth and characterized by sharp inflections at the end-points (*cf.* Fig. 1, curve D).

In the latter set of titrations the colour of quinquevalent tungsten was found to disappear exactly at the potentiometric end-point indicating that the end-point can be traced visually.

TABLE II

TITRATION OF W^{+5} WITH $0.01N$ BrO^{-3}

Acidity	*Normality of W^{+5}*	*Max. inflection per 0.1 ml mV*	*Theor. end-point ml*	*Exptl. end-point ml*	*Error %*
$10N$ HCl	0.00350	389	3.50	3.45	—1.43
$10N$ HCl	0.00510	399	2.55	2.53	—0.78
$9N$ HCl	0.00510	361	2.55	2.54	—0.39
$7.5N$ HCl	0.00510	378	2.55	2.54	—0.39
$3N$ HCl + $0.5N$ H_3PO_4	0.00840	286	4.20	4.19	—0.24
$2.5N$ H_3PO_4	0.00510	220	2.55	2.55	0.0
$2N$ H_3PO_4	0.00510	339	2.55	2.55	0.0
$0.5N$ H_3PO_4*	0.01136	361	4.40	4.39	—0.23

(*) Reverse titration.

C. Titration of ferricyanide

As was previously shown[6], the formal redox potential of the $[Fe(CN)_6]^{-3}/[Fe(CN)_6]^{-4}$ couple, amounts to 1.2 V. This value which is not in accordance with the theoretically known one[5] indicates that ferricyanide is a stronger oxidizing agent than ferric iron and that it can be quantitatively reduced by quinquevalent tungsten. The equilibrium constant and degree of completion for the reaction amount to $6.31 \cdot 10^{-33}$ and $7.94 \cdot 10^{-17}$ respectively.

The experimental results as shown in Table III A are equally accurate, whether the titration is performed in the presence of $0.5N$ to $5N$ H_3PO_4, 8-$9N$ HCl or in a mixture of both acids. The titration curves are also smooth and characterized by large jumps in potential, amounting to some hundred millivolts (curve B, Fig. 2).

The reaction which was carried out at room temperature takes place rapidly at the beginning of the titration but takes ~ 5 min at the end-point. It is noteworthy to remark that in the presence of 8-9N HCl, the reaction medium remains clear. When done in 0.5N H_3PO_4, the solution becomes turbid light brown and turns to whitish during the titration.

The titration of quinquevalent tungsten with ferricyanide, on the other hand (curve A, Fig. 2) is less advantageous. The error in this case may rise up to 1.2-1.6% and the time necessary for equilibrium is twice as long as in the reverse titration. However, the titration curves are smooth and possess sharp inflections.

TABLE IIIA

REDUCTION OF 0.01418N $[Fe(CN)_6]^{-3}$ WITH W^{+5}

Acidity	*Normality of* W^{+5}	*Max. inflection per 0.1 ml mV*	*Theor. end-point ml*	*Exptl. end-point ml*	*Error %*
0.5N H_3PO_4	0.01080	107	6.57	6.54	—0.46
0.5N H_3PO_4	0.00675	56	10.50	10.52	0.19
0.5N H_3PO_4	0.00639	52	5.55	5.54	—0.18
2N H_3PO_4	0.01080	49	6.57	6.58	0.15
5N H_3PO_4	0.01080	91	6.57	6.58	0.15
4N HCl + 1N H_3PO_4	0.00986	146	7.20	7.20	0.0
8N HCl	0.01071	41	6.63	6.62	—0.15
9N HCl	0.01071	60	6.63	6.63	0.0

TABLE IIIB

OXIDATION OF W^{+5} WITH 0.00893N $[Fe(CN)_6]^{-3}$

Acidity	*Normality of* W^{+5}	*Max. inflection per 0.1 ml mV*	*Theor. end-point ml*	*Exptl. end-point ml*	*Error %*
10N HCl	0.00437	171	4.9	4.9	0.0
2N HCl + 0.5N H_3PO_4	0.00441	134	4.94	4.93	—0.2
0.5N H_3PO_4	0.00384	35	4.3	4.25	—1.16

Titration of ferricyanide and ferric iron in a mixture

The formal redox potential of the ferri-ferrocyanide couple as evaluated from titration curves (curve A, Fig. 2) amounts to about 1.2 V. This value is higher than that of the ferric-ferrous system amounting to ~ 0.67 V[7]. This indicates that in a mixture of ferricyanide and ferric iron, the former will be reduced before the latter. The difference between the two potentials is sufficient to permit the separate titration of each constituent. The inflections at the ferricyanide stage are sharper than those of the ferric stage. This is confirmed experimentally as shown in Fig. 2, curve C. This curve represents the titration of a mixture containing 2.5 ml 0.01418N ferricyanide and 2.5 ml 0.00991N ferric iron, with 0.0059N W^{+5}. The experimental end-points amounting to 5.98 and 4.2 ml deviate only by —0.33 and 0.48% from the theoretical values.

Titration of dichromate and ferricyanide

In conformity with the high redox potential of the $[Fe(CN)_6]^{-3}/[Fe(CN)_6]^{-4}$ couple, it was not possible to titrate ferricyanide alone in a mixture with dichromate. The redox potentials of the Cr^{+6}/Cr^{+3} couple and the ferri-ferrocyanide system amount to $\sim$ 1.1 and 1.2 V, thus not differing much from each other. Reduction of both ferricyanide and dichromate takes place in one single step equal to the sum for the separate constituents (*cf.* Fig. 3, curve A). This curve represents the titration of a mixture containing 2.5 ml 0.01N $K_2Cr_2O_7$ and 2.5 ml 0.01278N ferricyanide in the presence of 2N HCl + 2N H_3PO_4 with 0.00847N W^{+5}.

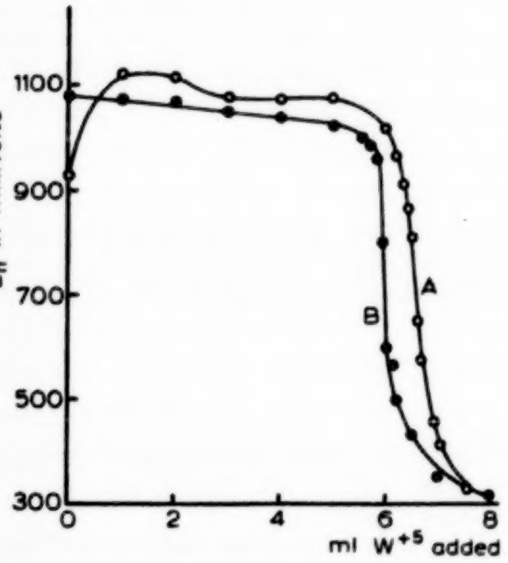

Fig. 3.

A. 2.5 ml 0.01N $K_2Cr_2O_7$ + 2.5 ml 0.01278N $K_3[Fe(CN)_6]$ in 2N HCl + 2N H_3PO_4 titrated with 0.00847N W^{+5} (in 10N HCl).
B. 2.5 ml 0.01N $K_2Cr_2O_7$ + 2.5 ml 0.01167N V^{+5} in 8N HCl titrated with 0.00912N W^{+5} (in 10N HCl).

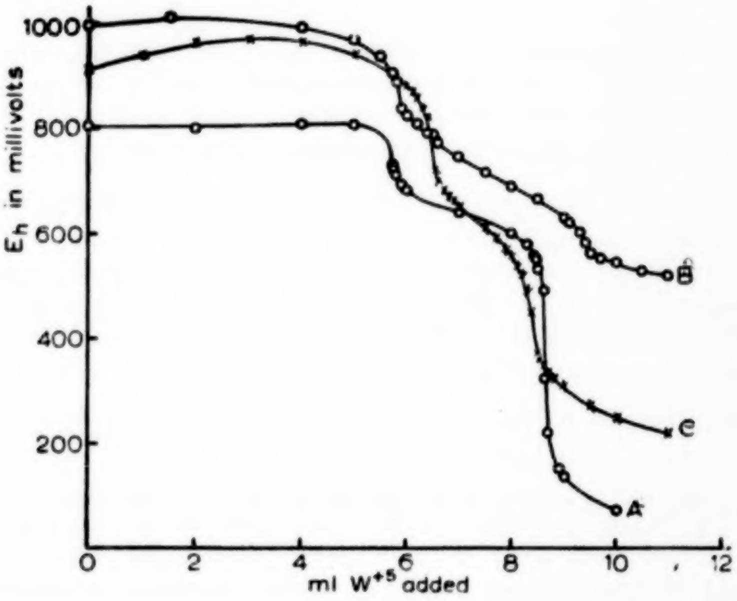

Fig. 4.

A. 5 ml 0.01N $K_2Cr_2O_7$ + 5 ml 0.05115N Fe^{+3} in 2N H_3PO_4 titrated with 0.00874N W^{+5} (in 10N HCl).
B. 5 ml 0.01196N V^{+5} + 5 ml 0.00718N Fe^{+3} in 0.2N H_3PO_4 titrated with 0.0102N W^{+5} (in 10N HCl).
C. 2.5 ml 0.01N $K_2Cr_2O_7$ + 2.5 ml 0.01167N V^{+5} + 2.5 ml 0.00667N Fe^{+3} in 0.5N H_3PO_4 + 0.5N HCl titrated with 0.0083N W^{+5} (in 10N HCl).

Titration of dichromate and vanadate

Similarly to the dichromate-ferricyanide mixture, the constituents of the dichromate-vanadate mixture are reduced simultaneously in one step. The titration curve (Fig. 3, curve B) is characterized by a single inflection, with the end-points corresponding to the sum of the separate end-points.

Titration of vanadate, dichromate and ferric iron

Mixtures of dichromate and ferric iron or vanadate and ferric iron on the other hand can be titrated in two separable steps. Like the ferricyanide-ferric mixture the titration curves possess two inflections; the first corresponding either to dichromate or vanadate whereas the second corresponds to ferric iron. In all cases the experimental end-points coincide fairly well with the calculated ones (*cf.* curves A and B, Fig. 4).

On titrating a mixture of dichromate, vanadate and ferric iron the titration curve possesses two inflections. The first inflection represents the simultaneous reduction of dichromate and vanadate while the second inflection represents the reduction of ferric iron alone. The experimental end-points coincide with the theoretical values. Fig. 4, curve C represents the titration of such a mixture when it contains 2.5 ml $0.01N$ $Cr_2O_7^{-2}$, 2.5 ml $0.01167N$ V^{+5} and 2.5 ml $0.00667N$ Fe^{+3}.

SUMMARY

Quinquevalent tungsten can be further applied as a reducing agent for the potentiometric estimation of ceric salts, ferricyanide and bromate. Reduction of these oxidants takes place easily when they are present alone or in mixtures containing them together with ferric iron, dichromate or vanadate.

RÉSUMÉ

Le tungstène(V) peut être utilisé comme réducteur pour le titrage potentiométrique des sels de cerium(IV), de l'anion ferricyanhydrique et de l'anion bromique. La réduction de ces oxydants s'effectue facilement, soit lorsqu'ils sont seuls, soit lorsqu'ils sont mélangés au fer(III), à des bichromates ou à des vanadates.

ZUSAMMENFASSUNG

Fünfwertiges Wolfram kann auch als reduzierendes Mittel für die potentiometrische Bestimmung von Cer(IV)-Salzen, Ferricyanid und Bromat verwendet werden. Die Reduktion dieser Oxydationsmittel verläuft leicht wenn sie allein oder in Mischungen mit Ferri-Eisen, Dichromat oder Vanadat vorhanden sind.

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A POLAROGRAPHIC STUDY OF THE COMPLEXES OF PONTACHROME VIOLET SW*

by

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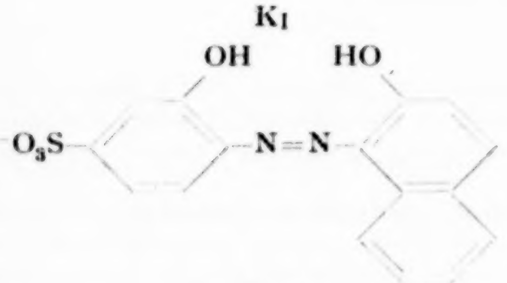
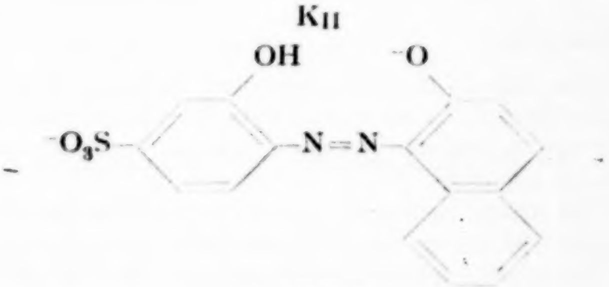
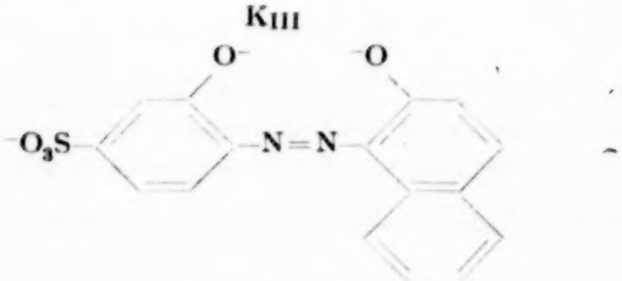
The azo dye Pontachrome Violet SW (I) is readily reduced at a dropping mercury cathode. If the dye solution contains aluminum, part of the diffusion wave is displaced and appears as a distinct second wave, although the total diffusion current remains constant. The height of the second wave was found by WILLARD AND DEAN[1] to be proportional to the concentration of aluminum in the solution. This relationship enabled these authors to develop a unique method for determining aluminum. At the optimum acidity (pH = 4.65) for the determination of aluminum, it was found that alkaline earth cations, with the exception of beryllium, caused precipitation of the dye and thus could not be tolerated. However, SCHWARZENBACH AND BIEDERMANN[2,3] have described soluble complexes of calcium, magnesium, strontium, zinc and cadmium with very similar azo dyes in the pH range 8 to 11. Thus, it was thought that a polarographic study of the complexes of Pontachrome Violet SW in basic solutions might reveal interesting analytical applications.



I (H_2F^-).



II (HF^{-2}).



III (F^{-3}).

Pontachrome Violet SW (C.I. 169) and the ligands resulting from the stepwise removal of a proton.

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[*] From a portion of the Ph.D. Dissertation of H. ALDEN BRYAN, University of Tennessee, August, 1955.

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The study was limited to the complexes of those cations which do not precipitate in the buffer systems employed. All of the complexes studied gave a displacement of the polarographic wave of the dye. The polarograms obtained are illustrated in Fig. 1 by the Magnesium-Violet SW system. None of the alkali metal ions, nor barium and strontium, form complexes in the pH range studied.

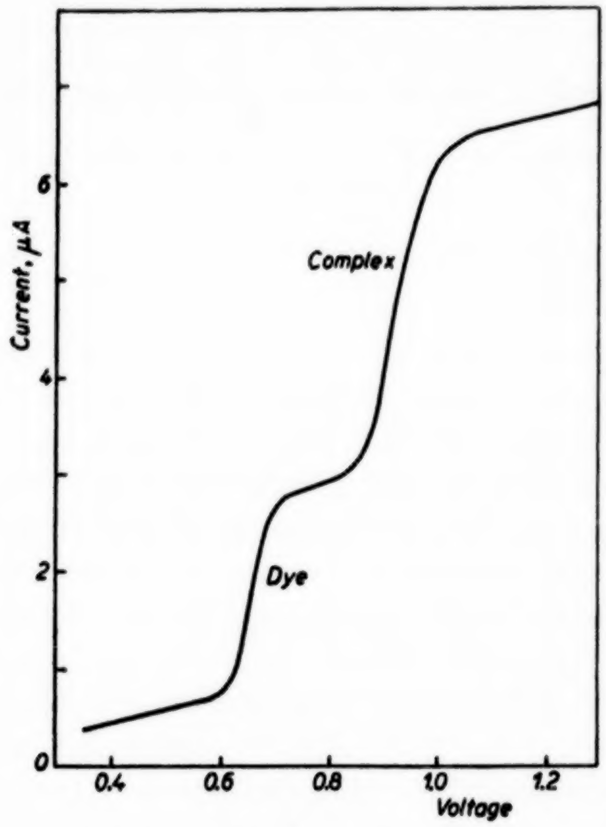

Fig. 1.

APPARATUS AND REAGENTS

Materials

The impure dye was obtained from Du Pont de Nemours and Company. Purification of the dye was effected by recrystallization from acetone-ether mixtures. Further recrystallization caused no change in absorption spectrum nor in polarographic behavior. The recrystallized dye was thus assumed pure.

Eastman, technical grade, piperidine was used without purification. Although it was faintly yellow in color, its solutions gave no polarographic wave in the voltage range studied.

Standard solutions of metal ions were prepared from reagent grade metal salts. Buffer solutions were also prepared from chemically pure reagents.

Apparatus

All measurements were made using a Sargent-Heyrovsky model XII recording polarograph, at 25.0 ± 0.4° C, using a saturated calomel electrode of low resistance as a reference electrode. The maximum error in potential readings due to resistance of the reference electrode was 0.005 volt.

All pH measurements were made with a Beckman model G pH meter.

EXPERIMENTAL

Study of the Pontachrome Violet SW solutions

A series of solutions was prepared by mixing 20.00 ml of standard Violet SW solution and 10 ml of $2M$ ammonium chloride solution, adjusting each mixture to the desired pH with $6M$ sodium hydroxide and diluting to 50 ml in a volumetric flask.

A second series of solutions was prepared by measuring 20.00 ml of standard Violet SW solution and 1.5 ml of piperidine. Each mixture was adjusted to the desired pH with 6M hydrochloric acid and diluted to 50 ml as before. The data in Table I show that the diffusion current constant, I_d, does not depend on the buffer used.

TABLE I

DIFFUSION CURRENT CONSTANT OF VIOLET SW

Each solution was 0.360 mM in Violet SW. $m^{2/3}t^{1/6}$ was 3.03 in ammonia buffers and 3.05 in piperidine buffers. $I_d = \dfrac{i_d}{Cm^{2/3}t^{1/6}}$.

pH	i_d (μA)	I_d
In ammonia buffers		
7.95	5.76	5.28
8.00	5.76	5.28
8.15	5.76	5.28
8.52	5.72	5.24
8.55	5.76	5.28
8.65	5.82	5.33
9.00	5.64	5.17
9.05	5.70	5.22
9.15	5.70	5.22
	Average	5.26 ± 0.06
In piperidine-hydrochloric acid buffers		
10.00	5.62	5.12
10.00	5.64	5.14
10.40	5.48	4.99
10.50	5.70	5.19
11.10	5.53	5.03
11.40	5.48	4.99
11.60	5.36	4.88
11.65	5.70	5.19
	Average	5.07 ± 0.09

The half-wave potential of the dye is a linear function of pH in the range of 8 to 12, and can be represented by the following equation:

$$E_{1/2} = -0.035 - 0.060 \text{ pH} \qquad (1)$$

In the pH range 3 to 5 a linear relationship was also obtained:

$$E_{1/2} = 0.100 - 0.089 \text{ pH} \qquad (2)$$

This means that the dye species existing in basic solutions (II) is more difficult to reduce than the species in acid solutions (I). This is to be expected since the form in basic solution bears one more negative charge than the form in solutions of pH 3 to 5. Ionization of the dye occurs in the pH range 5.5 to 7.5; polarograms obtained in this range are not reproducible.

Time studies

At a pH of 4.6 the aluminum complex forms very slowly at room temperature[1]. Thus it was deemed necessary to find the effect of time of standing on the polarographic waves in basic solution. Solutions of pH 9.0 were prepared as described in the preceding section, and several drops of a 0.1M solution of aluminum were added.

Polarograms were run immediately and after periods of one and three hours. This procedure was repeated using the other cations studied. Neither the diffusion currents nor the shapes of the waves were altered by standing. It was concluded that equilibrium is attained very quickly in a basic solution.

The aluminum complex

A series of solutions was prepared containing accurately measured quantities of Violet SW and standard aluminum solutions, and 10 ml of 2*M* ammonium chloride solution. These mixtures were adjusted to the desired pH in the range 8 to 9.8 with 6*M* sodium hydroxide solution and diluted to 50 ml in a volumetric flask[5]. A second series of solutions was prepared by mixing accurately measured quantities of Violet SW and standard aluminum solutions, adding 1.5 ml of piperidine, adjusting to the desired pH in the range 10 to 12 with 6*M* hydrochloric acid and diluting to 50 ml in a volumetric flask. The data obtained from the polarograms of these solutions and some calculated quantities are given in Table II. The diffusion current constant, I_d, was calculated in the usual manner[4], using the concentration of cation added as the concentration of the complex. The quantity m represents the number of dye molecules per aluminum ion in the complex, and was calculated by

TABLE II

POLAROGRAPHIC DATA FOR THE VIOLET SW ALUMINUM COMPLEXES

Each solution was 0.360 m*M* in Violet SW

Aluminum concentration (mM)	*pH*	*Second wave* i_d *(μA)*	$m^{2/3}t^{1/6}$ $(mg^{2/3}sec^{-1/2})$	I_d	*Total* i_d *(μA)*	m
0.0742	8.00	2.71	3.03	12.1	5.16	2.54
0.0742	8.50	3.16	3.03	14.6	5.36	2.87
0.0742	9.05	3.16	3.03	14.6	5.22	2.90
0.0742	9.65	2.65	3.03	12.8	5.23	2.34
0.223	10.10	2.65	3.38	3.51	5.36	0.80
0.223	10.40	1.30	3.38	1.72	5.20	0.40

$$m = \frac{(\text{second wave } i_d)\ (\text{dye concn.})}{(\text{total } i_d)\ (\text{aluminum concn.})} \quad \ldots\ldots\ldots\ldots \quad (3)$$

It is seen that m reaches a maximum of about 3 for the aluminum complex at the lower values of pH. Hydroxyl ion probably competes with the dye anion for the aluminum ion at higher pH values.

The half-wave potential of the aluminum complex is represented by

$$E_{1/2} = -0.234 - 0.050 \text{ pH} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (4)$$

WILLARD AND DEAN reported the relation

$$E_{1/2} = -0.258 - 0.058 \text{ pH} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (5)$$

for the pH range 3 to 5. This is close enough agreement to indicate that there must be very little difference if any in the structure of the complex in the two pH ranges.

References p. 93.

Other metal-dye complexes

Solutions were prepared as in the study of the aluminum complex, substituting accurately measured quantities of standard solutions of other cations for the aluminum solution. The solutions were de-aerated with nitrogen for fifteen minutes before recording the polarograms. The results are given in Table III. Quantities in this table were calculated in the manner as for the aluminum complex.

TABLE III

COMPLEXES OF PONTACHROME VIOLET SW

Each solution was 0.360 m*M* in Violet SW. $m^{2/3}t^{1/6}$ was 3.05 in ammonia buffers and 3.38 in piperidine buffers.

pH	I_d	*m*
Zinc complex: each solution 0.119 m*M* in zinc ion		
7.85	7.02	1.29
8.45	7.02	1.25
9.05	6.68	1.18
9.55[a]	6.98	1.18
10.10[b]	7.55	1.81
10.55	8.61	2.07
11.20	9.51	2.37
Cadmium complex: each solution 0.137 m*M* in cadmium ion		
8.05	4.33	0.83
8.50	4.57	0.87
9.00	4.93	0.94
9.45	5.20	0.99
9.92[a]	5.46	1.04
Iron(II) complex: each solution 0.0896 m*M* in iron(II) ion		
7.95	5.61	1.06
8.52	5.61	1.06
9.15	5.70	1.07
9.65[a]	4.35	0.85
10.25[b]	1.43	0.36
10.95	0.80	0.18
11.50	0.80	0.20
Nickel complex: each solution 0.0557 m*M* in nickel ion		
8.00	10.0	1.91
8.55	10.7	2.03
9.05	11.4	2.22
9.55[a]	12.0	2.27
10.00[b]	13.8	2.98
10.50	14.4	3.07
11.10	13.8	3.04
11.60	14.6	3.30
Cobalt(II) complex: each solution 0.100 m*M* in cobalt(II) ion		
7.95	14.5	2.80
8.55	13.9	2.68
9.10	14.9	2.91
9.50[a]	13.3	2.68
10.15[b]	9.67	2.22
10.50	11.35	2.60
11.00	10.70	2.43
11.55	6.68	1.53
Magnesium complex: each solution 0.303 m*M* in magnesium ion		
9.00	0.24	0.05
9.00	0.50	0.09
9.50	0.85	0.16
9.70[a]	1.84	0.34
10.00[b]	2.78	0.61
10.40	3.31	0.73
10.70	3.97	0.80
10.90	3.88	0.85
11.40	4.29	0.96
11.65	4.45	0.96
Manganese(II) complex: each solution 0.1074 m*M* in manganese(II) ion		
8.05	2.70	0.56
8.60	4.16	0.88
9.00	5.60	1.19
9.50	6.48	1.38
9.85[a]	6.07	1.60
10.00[b]	7.73	1.69
10.45	7.82	1.98
10.90	9.92	2.53
11.50	9.98	2.70

[a] Ammonia buffer
[b] Piperidine buffer

I_d and m for the zinc complex are essentially constant in ammonia buffers but increase with pH in piperidine buffers. The maximum number of ligands per zinc ion, about 2, is that expected for a bidentate ligand with an ion of common covalence of 4. The half-wave potential of the complex is represented by

$$E_{1/2} = -0.356 - 0.046 \text{ pH} \qquad (6)$$

The pH range was only 8 to 10 for the cadmium complex since the complex is not formed in the presence of piperidine. I_d and m values increase slightly with pH, but the maximum number of ligands per cadmium ion, about 1, indicates either competition for two positions in the normal covalency of 4 or that the dye is behaving as a tridentate ligand. The half-wave potential of the complex is given by

$$E_{1/2} = -0.318 - 0.047 \text{ pH} \qquad (7)$$

The maximum number of ligands in the iron(II) complex is about 1 at the lower pH values. Hydroxyl ion probably competes for the iron at higher pH values. The half-wave potential of the complex is given by

$$E_{1/2} = -0.128 - 0.073 \text{ pH} \qquad (8)$$

The nature of the nickel complex depends almost entirely on the nature of the buffer. Both I_d and m are nearly constant in solutions containing the same buffer ingredients. The number of ligands per nickel ion is about 2 in ammonia buffers and 3 in piperidine buffers. Nickel(II) ordinarily has a covalency of either 4 or 6. The half-wave potential of this complex is represented by

$$E_{1/2} = -0.389 - 0.055 \text{ pH} \qquad (9)$$

The data for the cobalt(II) complex is a little uncertain since the first wave is poorly formed and the beginning of the second wave is difficult to see. Nevertheless, it is believed accurate to within about 5 per cent. The total diffusion current in ammonia buffers is too high. This is probably due to the formation of some cobalt(III) hexammine complex, which is reduced at about −0.5 volt *vs* S.C.E.[5] For the calculation of m values the total i_d was estimated to be the same as obtained for the nickel complex. I_d and m values in ammonia buffers are nearly constant, and in piperidine solutions are somewhat smaller. This probably means competition by piperidine molecules for the cobalt ions. The maximum m value, nearly 3, is that expected for cobalt. The half-wave potential of the complex is given by

$$E_{1/2} = -0.344 - 0.053 \text{ pH} \qquad (10)$$

Both I_d and m for the magnesium complex increase with increasing pH. The maximum m value of about 1 may be contrasted with reported 2 to 1 and 3 to 1 complexes of Eriochrome Black T with magnesium ion[6]. However, if it is assumed that the metal ion coordinates with the completely ionized dye molecule (F^{-3}), the increased complex formation at higher pH is expected. Furthermore, in solutions of the same pH Eriochrome Black T would be expected to form a higher complex since its final ionization constant ($K_{III} = 11.55$)[3] is considerably lower than that of Pontachrome Violet SW ($K_{III} > 12.4$).

An attempt was made to study Eriochrome Black T in basic solution on the polarograph. The reduction waves showed maxima which could not be removed by the addition of gelatin or other maximum suppressors. The investigation was not pursued further.

The half-wave potential of the Violet SW-magnesium complex is given by

$$E_{1/2} = -0.122 - 0.077 \text{ pH} \quad (11)$$

For the manganese (II) complex both I_d and m increase with pH. The maximum m has apparently not been attained at pH 11.5 but appears to be approaching 3. This is the expected maximum since the common coordination number of manganese(II) is 6. The half-wave potential is given by

$$E_{1/2} = -0.237 - 0.057 \text{ pH} \quad (12)$$

CONCLUSIONS

All of the Violet SW complexes studied gave a second wave whose height was proportional to the amount of complexing cation present. Thus analytical procedures for these cations could be developed. An amperometric method for magnesium is described in a subsequent publication.

SUMMARY

In a polarographic study of the aluminum, iron(II), cobalt(II), nickel, zinc, cadmium, manganese(II), and magnesium complexes with Pontachrome Violet SW, a 2,2′-dihydroxyazo dye, it was found that each complex produced a wave at more negative potentials than the dye alone. Values for the diffusion current constant, I_d, for each complex were calculated from data obtained for alkaline solutions. Calculations of the ratio of dye molecules to each cation gave maximum values corresponding to expected values based on the usual coordination number of the cation and a bidentate ligand.

RÉSUMÉ

Lors de l'étude polarographique des complexes de l'aluminium, du fer(II), du cobalt(II), du nickel, du zinc, du cadmium, du manganèse(II) et du magnésium avec le violet pontachrome SW (colorant 2,2′-dihydroxyazoïque), on a constaté que chacun de ces complexes donnait une vague à des potentiels plus négatifs que le colorant seul. Les valeurs de la constante du courant de diffusion, I_d, pour chaque complexe ont été calculées à partir des données obtenues pour des solutions alcalines. Les calculs du rapport des molécules de colorant avec chacun des cations ont donné les valeurs maximums correspondant aux valeurs prévues en se basant sur le nombre de coordination usuel entre le cation et un composé complexé bivalent.

ZUSAMMENFASSUNG

Bei der polarographischen Untersuchung der Komplexe von Aluminium, Eisen(II), Kobalt(II), Nickel, Zink, Kadmium, Mangan(II) und Magnesium mit Pontachromviolett SW (einem 2,2′-Dihydroxyazo-Farbstoff) wurde festgestellt, dass jeder dieser Komplexe eine Welle bei negativeren Potentialen gibt, als der Farbstoff allein. Die Werte der Diffusionsstromkonstante, I_d, wurden für jeden Komplex aus mit alkalischen Lösungen erhaltenen Werten berechnet. Das Verhältnis der Anzahl Farbstoffmoleküle zu jedem Kation wurde berechnet und die erhaltenen Maximumwerte stimmten mit den auf Grund der gewöhnlichen Koordinationszahlen der Kationen mit einem „zweizähnigen" Ligand zu erwartenden Werten überein.

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THE NATURE OF THE COMPLEXES OF 2.2′-DIHYDROXYAZO COMPOUNDS*

by

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So far as is known, complexes of 2.2′-dihydroxyazo compounds are the only recorded cases in which a metal-organic compound results in a polarographic wave which is discretely different from the wave of the organic compound alone. In this investigation an attempt was made to determine what special structural features cause the unusual polarographic behavior.

Evidence that the polarographic reduction of an azo-group involves two electrons and that hydrazo compounds are the reduction products was obtained by SHIKATA AND TACHI[1], and NGA[2]. The reduction may be represented as

$$\text{R—N=N—R} + 2\,\text{H}^+ + 2\,e \rightarrow \text{R—NH—NH—R}$$

Studies using platinized platinum electrodes indicate that the azobenzene-hydrazobenzene system is reversible[3]. Polarographic work has not been extensive enough to decide whether this is true at the dropping electrode[4]. If so, the half-wave potential of the system should be given by the following equation:

$$E_{1/2} = E^\circ + 0.030\,K' - 0.059\ \text{pH}$$

where K' is the logarithm of the ratio of the diffusion coefficients of the azo- and hydrazo-compounds. This ratio might be expected to be close to unity, and thus render K' negligible. For azobenzene SHIKATA AND TACHI[1] found the reduction involved hydronium ions, but they did not obtain a linear relation between pH and reduction potential. On the other hand VOLPI[5] reported that the half-wave potential was independent of pH. HILLSON AND BIRNBAUM[6] have shown, however, that below a pH of 8.5 a linear relation is obtained. Their results for azobenzene were confirmed by CASTOR AND SAYLOR[7], whose experimental relation is

$$E_{1/2} = 0.060 - 0.062\ \text{pH}$$

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Structures for Pontachrome Violet SW (C.I. 169) similar to those proposed for Eriochrome Black T by SCHWARZENBACH[8] are presented in structures (I), (II) and (III); In order to simplify the discussion, these structures will frequently be represented by H_2F^-, HF^{-2}, and F^{-3}, respectively (see previous paper, p. 87).

POLAROGRAPHIC EVIDENCE

Polarographic data for Violet SW complexes have been reported[9]. DEAN[10] has given data for Pontachrome Blue-Black R (C.I. 202) and its aluminum complex. For the pH range 3 to 5 the half-wave potential is given by

$$E_{1/2} = 0.075 - 0.081 \text{ pH}$$

for the dye alone, and by

$$E_{1/2} = -0.256 - 0.058 \text{ pH}$$

for the Blue-Black R-aluminum complex. A straight line relationship is also obtained for this dye in the pH range 7.5 to 9.5:

$$E_{1/2} = -0.32 - 0.061 \text{ pH}$$

The midpoint of the discontinuity between pH 5.8 and 7.7 corresponds rather closely to the pK_2 value for this dye as reported by SCHWARZENBACH AND BIEDERMANN[8] and confirmed in our laboratory in a spectrophotometric investigation. Measurements at pH values higher than 9.5 were unobtainable because of the dye's slight solubility.

The discontinuity observed for Violet SW is between pH 5.6 and 7.6. pK_2 for Violet SW might reasonably be expected to be about 6.6. Solutions of Violet SW at pH 12.4 using piperidine as the base exhibited no color change, whereas solutions made basic with sodium hydroxide of pH 12 and above were red as if a complex had formed. Nevertheless, pK_3 for Violet SW must be well above 12.4 whereas SCHWARZENBACH AND BIEDERMANN reported a value of 11.5 for Blue-Black R. The pK_3 value for Eriochrome Black T is also 11.5, which explains the greater number of dye molecules per cation in Eriochrome Black T complexes than in Violet SW complexes at the same pH. That is, if we assume that magnesium and calcium react only with the completely ionized dye molecule (F^{-3}), the observed equilibria are clear. More easily complexed ions are able to react with the HF^{-2} ions, and thus form complexes in basic solution but not in solutions of pH lower than about 6. Such ions are zinc and cadmium. Cations easily complexed are able to react with the HF^{-2} ion. These include nickel, cobalt(II), chromium(III), iron(II) and (III), and copper(II). Aluminum is evidently between this group and the zinc-cadmium since it does form the complex in acid solutions, but the reaction takes about 4 hours to reach equilibrium at pH 4.2 and room temperature. At pH 4.7 only one hour was required. It is therefore apparent that hydroxyl ion exerts a very great effect on the complex formation. Two effects would be expected: (1) As the pH of the system rises, the aquated aluminum ion undergoes appreciable hydrolysis; and (2) the concentration of the dye anions increases. The first factor must be relatively unimportant since the influence of aluminum concentration upon the reaction rate is small. The influence of temperature on the reaction rate is marked since at 60°C and pH 4.6 the reaction is complete after only 5 minutes.

The hydrogen ion concentration affects the magnitude of the diffusion current constant for the aluminum complex[10]. WEISSLER AND WHITE observed a similar pH dependency in their fluorometric method for aluminum in which these same azo dyes were used[11]. A decrease in diffusion current is observed for pH values less than 4.0, but the rapid increase in the magnitude of the diffusion current constant above pH 5.0 finds no parallel in the fluorometric work. The reason for the increase in diffusion current constant for the aluminum-complex is discussed later. The explanation for the decrease in fluorescence above pH 5 as found by WEISSLER AND WHITE is to be found in the absorption spectra of the dye and aluminum-complex and the fluorescent spectrum of the complex. When excited by mercury arc radiation the aluminum complex with Violet SW fluoresces strongly in the 560 to 620 mμ region. The dye anion in solutions of pH 5 or less absorbs strongly in the 440 to 560 mμ region. In solutions of higher pH the HF^{-2} dye anion absorbs strongly in the 480 to 620 mμ region. Since WEISSLER AND WHITE maintained an excess of dye in all solutions it is apparent that absorbance of the fluorescence of the complex by the excess dye is responsible for the observed data.

Two of the cations which interfere with the determination of aluminum by the WILLARD-DEAN method[12], titanium(IV) and vanadium(V), give a metal-dye wave which can be distinguished from both the original dye and the aluminum-dye wave. This differentiation is possible only when the aluminum and titanium (or vanadium) are present in a molar ratio of about unity. The titanium wave is displaced only about 0.14 volt whereas the aluminum wave is displaced about 0.25 volt from the wave of the dye itself. The titanium wave height is proportional to the amounts of titanium present.

No double polarographic wave is obtained with mono-*ortho*-hydroxyazo dyes. Those investigated include Orange II (the monohydroxy analogue of Pontachrome Violet SW), Orange GG, and Amaranth.

RADLEY[13] has reported fluorescence with aluminum ion in the presence of eight different dyes, all of whom possessed 2.2'-dihydroxyazo structures. For maximum stability two metallizable groups are apparently needed in the positions *ortho* to the azo linkage, at least one of which should be hydroxyl. The other can be an amino, carboxyl, or a second hydroxyl group.

CIS-TRANS ISOMERS

Logical extension of the tetrahedral nitrogen structure leads to the prediction that *cis-trans* azo isomers should be encountered. These isomers have in fact been isolated for azobenzene by HARTLEY[14]. WINKEL AND SIEBERT[15] found the half-wave potential for the polarographic wave of *cis*-azobenzene to be —0.68 volt *vs* S.C.E. while that of *trans*-azobenzene occurred at —0.92 volt, a difference of 0.24 volt. Only the *trans* wave proved stable on standing, and it increased in height as the second wave decreased. In the present investigation a difference of 0.25 volt was found between the wave of the dye alone and the wave of the aluminum-dye complex. Thus, it seems quite reasonable to conclude that *cis-trans* transformations might be involved in the aluminum-dye complex wave.

THE POLAROGRAPHIC REACTION

Analysis of the individual polarographic waves for the dye and the complex yields valuable information concerning the reversibility of the electrode reaction

References p. 100.

and the number of electrons involved both in the rate determining step and in the overall reduction. If log $(i_d - i)/i$ is plotted against the corresponding values of the potential of the dropping electrode, a straight line should be obtained. Furthermore, the line should have a slope approximately equal to $0.059/n$ where n is the number of electrons involved in the reversible reduction. DEAN[10] plotted data for Violet SW and also for the two waves obtained with Violet SW in the presence of aluminum at pH 4.6. Good straight lines were obtained, indicating possible reversibility. The slopes of the dye wave itself and of the first portion of the combined wave (uncomplexed dye) are 0.065 and 0.053, respectively. The slope of the second part of the combined wave (the aluminum-dye complex), however, is 0.042. Similar data for the Violet SW wave at pH 8.5 gave a slope of 0.054. Since the hydrazo compound is the expected reduction product for the dye molecules in each instance, the number of electrons should be two and the slope should therefore be 0.030. Thus, it is probable that the potential determining step in the reduction of the dye alone is the reversible addition of one electron. The reduction of the aluminum complex appears to be irreversible.

COMPOSITION OF THE COMPLEXES

The number of dye molecules present in a molecule of each complex with eight different cations has been calculated previously by the molar ratio method[9]. These values are only approximate since two assumptions were made in those calculations: (1) that the total wave height for the dye reduction is the same whether the dye is in a complex or free, and (2) that all of the metal ion placed in the solution was present in the complex. The first assumption is based on experimental observation and is probably correct. The second assumption is obviously incorrect for some of the solutions of some of the cations studied; for example, iron(II) at pH 10.5 where precipitation probably occurred. The maximum m-value observed for the complexes of a given cation may be assumed with a great deal more confidence to represent a solution which contained all of that particular metal in a complex with the dye. These maximum m-values for the most part agree with known maximum "coordination numbers" for the cations if the dye is assumed to be bidentate.

Another way to determine if these m-values are reasonable is to calculate the diffusion coefficients of the complexes from the polarographic data, and taking the number of electrons involved as m times the number required for the reduction of one molecule of the dye alone. All studies of azo compounds with the dropping mercury electrode have shown that 2 electrons are involved in the reduction of each molecule. Therefore, assuming a 2-electron change the diffusion coefficient of the dye was calculated to be $1.83 \cdot 10^{-5}$ cm^2/sec. The value agrees with a value of $1.84 \cdot 10^{-5}$ cm^2/sec found for stilbene, a molecule of similar size and structure[16]. The diffusion coefficients of the complexes calculated from the observed I_d, and using $2m$ as the number of electrons for each complex, are given in Table I. All values appear to be reasonable although data for comparable complexes are not available in the literature for comparison. The data for aluminum at pH 4.65 are based on the diffusion current constant given by WILLARD AND DEAN[12], and a consideration of molar ratios and polarographic data by DEAN[10]. The second wave given by a solution containing $7.2 \cdot 10^{-6}$ moles of aluminum and $16 \cdot 10^{-6}$ moles of Violet SW was exactly the same height as the first wave. Thus about half of the dye must have been in the

TABLE I

DIFFUSION COEFFICIENTS FOR VIOLET SW COMPLEXES

Cation complexed	*Maximum* i_d	*Approximate pH*	*Number of electrons (2m)*	$D \times 10^5$, $cm^2/sec.$
None	5.18	8-12	2[b]	1.83
Aluminum	5.09[c]	4.65[c]	2[c]	1.75
Aluminum	14.8	8	6	1.65
Zinc	9.51	11	4	1.54
Cadmium	5.46	10	2	2.03
Iron(II)	5.70	9	2	2.21
Nickel	12.0	10	4	2.44
Nickel	14.6	11	6	1.61
Cobalt(II)	14.9	9	6	1.67
Cobalt(II)	11.4	10.5	6	0.95
Manganese(II)	9.98[a]	11.5	6	0.79
Magnesium	4.45[a]	11.5	2	1.35

[a] I_d for these complexes increases with pH without giving a maximum value.
[b] Assumed value on which Table is based.
[c] From Reference 12.

complex, giving a ratio of 7 aluminum to 8 dye molecules, or *m* is about 1. WEISSLER AND WHITE extracted the Pontachrome Blue-Black R-aluminum complex with *n*-amyl alcohol and found upon analysis a 2 to 1 ratio. However, the pH was 5.0, which represents a higher I_d for the aluminum-Violet SW complex, indicating the addition of another dye molecule to the complex at about this pH. Also, Blue-Black R forms a more stable complex with magnesium than Eriochrome Black T, which in turn complexes more readily with magnesium than does Violet SW[17,18]. Thus Blue-Black R might be expected to complex more readily with aluminum than Violet SW, especially at a higher pH.

DISCUSSION

The composition of the complexes has been discussed. The remaining problem is the reason for the polarographic behavior of the complexes. Four explanations are considered:

(1) Stabilization of the *cis* isomer of the dye through complex formation. The basis for this proposal is the reported observation that azobenzene and some of its derivatives exhibit a polarographic wave for the *cis* isomer which is displaced about 0.2 volt from the wave of the *trans* isomer. According to CASTOR AND SAYLOR[7] only one wave is produced under polarographically reversible conditions. The solutions in this investigation were well buffered to assure an ample source of hydrogen ions for reversibility. In every case reported in the literature, the *cis* isomer was more easily reduced than the *trans* form. For the aluminum-dye complex it would have to be assumed that the *cis* isomer is the form stabilized, yet the complex is more *difficult* to reduce than the dye alone. Thus the *cis-trans* explanation is unsatisfactory unless the assumption is made that the dye molecule is held rigidly in the *cis* position, perhaps throughout the reduction, and that this rigidity is sufficient to enable the reduction potential to be shifted to a value more negative than that of the free dye. The latter proposal will be considered subsequently.

(2) Stabilization of an anionic form of the dye similar to the proposal of Costa[19]. An anionic form of the dye could be more difficult to reduce than the parent molecule. This explanation does not seem appropriate since the dye used in this work did not exhibit a second wave at higher pH values except in the presence of a complexing cation.

(3) Interference with azo reduction by coordination. The proposal that the azo group may coordinate to a suitable cation is not original. In fact, 2.2'-dihydroxyazo compounds have been proposed as possible tridentate ligands by Jonassen and DeMonsabert[20]. Thus one might propose interference by the cation during reduction of the azo linkage because of coordination of the azo group to the cation. The fact that nearly all complexable cations give a similar wave supports this proposal. A consideration of Table III in reference[9] reveals that a number of cations show a maximum coordination number in the Violet SW complexes, considering the dye as a bidentate ligand. It has already been shown that the presence of both hydroxyl groups is necessary for complex formation[21] as well as for the polarographic behavior. In these complexes Violet SW cannot be tridentate, yet the same polarographic behavior is observed. Therefore azo coordination is not the cause.

(4) Interference with normal azo reduction by the rigidity of the complex. The dye alone seems to add only one electron reversibly, whereas the complexed dye adds two. The difference may possibly be caused by the strain on the azo group in the complex. The size of the complexing cation ought to be a factor, causing varying amounts of strain in the complex. Table II correlates the ionic radius of the cation[22] in the complex with the shift in half-wave potential of the complex. The trend is quite good except for aluminum. Possibly a covalent radius should be used for aluminum (1.26 Å)[23], or perhaps relatively large and relatively small ions could complex without causing much strain.

TABLE II

THE SHIFT IN HALF-WAVE POTENTIAL OF THE COMPLEX AND THE IONIC RADIUS OF THE COMPLEXING CATION

Cation	*Shift in half-wave potential* [a] *volt*	*Ionic radius* [22] *Å*
Aluminum	0.11	0.57
Cadmium	0.15	1.03
Manganese(II)	0.17	0.91
Zinc	0.18	0.83
Iron(II)	0.22	0.83
Cobalt(II)	0.23	0.82
Magnesium	0.25	0.78
Nickel	0.30	0.78

[a] Calculated for pH 10 from equations in Reference 9.

Possibly after the addition of one electron to the dye alone, a semi-stable ion is formed in which all the nitrogen bonds are tetrahedral. Since the rigid complex is unable to revert to this state the potential must be greater in order to force two electrons to be taken by the azo group at the same time.

To summarize this discussion one may say that no definite conclusion is possible as yet although a number of possible explanations have been proved incorrect.

The most likely cause of the polarographic behavior is the rigidity of the complex compared with the flexibility of the free dye anions. This explains satisfactorily why all complexing cations cause the phenomenon, the relative difficulty of reduction of the various complexes, the compositions of the complexes, and the fact that the half-wave potential of the complex does not seem to depend on the number of dye molecules in the complex.

SUMMARY

The metal complexes of Pontachrome Violet SW, a di-*ortho*-dihydroxyazo type dye, were studied in an attempt to deduce a reason for the unusual polarographic behavior such as gave rise to the WILLARD-DEAN method for aluminum. *Cis-trans* isomers, anionic species and azo coordination to the central cation are ruled out. The most likely cause seems to be the rigidity of the complex with the result that the reduction of the complex occurs by a different mechanism then the reduction of the free dye.

RÉSUMÉ

Les complexes métalliques du violet pontachrome SW (colorant du type di-*ortho*-dihydroxyazoïque) ont été étudiés pour essayer d'expliquer le comportement polarographique anormal qui a permis l'établissement de la méthode de WILLARD-DEAN pour le dosage de l'aluminium. Les isomères *cis-trans*, les formes anioniques et les azo-coordinations sur le cation central ont été envisagés et écartés. La cause la plus vraisemblable semble être la rigidité du complexe, qui fait que le mécanisme de la réduction du complexe est différent de celui du colorant libre.

ZUSAMMENFASSUNG

Die Metallkomplexe des Di-*ortho*-dihydroxyazo-Farbstoffes Pontachromviolett SW wurden untersucht um ihr ungewöhnliches polarographisches Verhalten zu erklären, auf welches sich zum Beispiel die Aluminium-Methode von WILLARD-DEAN gründet. *Cis-trans*-Isomerie, anionische Formen und Azo-Koordinationen zu dem zentralen Kation konnten ausgeschaltet werden. Die wahrscheinlichste Ursache scheint die Steifheit des Komplexes zu sein, welche verursacht, dass die Reduktion des Komplexes nach einem anderen Mechanismus stattfindet als die des freien Farbstoffes.

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STUDIES ON COORDINATION COMPOUNDS

XVI. FORMATION CONSTANTS OF SOME METAL SALTS OF THE NITROSONAPHTHOLS

by

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INTRODUCTION

1-Nitroso-2-naphthol and less commonly, 2-nitroso-1-naphthol, have long been employed as precipitating reagents for cobalt. These reagents are particularly useful to the analytical chemist as a means of separating cobalt from nickel[1]. However, the *o*-nitrosonaphthols are not specific for cobalt but form coordination compounds with many other metals. The extreme insolubility in aqueous solution of these ligands and their metal salts enhance their usefulness as dyes, but discourage the study of the complex equilibria involved. CALVIN AND WILSON[2] showed that it was possible to study the equilibria of water-insoluble chelates by using a 50% dioxan-water solvent system. VAN UITERT *et al.*[3,4] extended this work to cover all practical concentration ranges of dioxan-water solvent systems by introducing a method for determining the thermodynamic equilibrium constants and by providing suitable correction data for calculating such constants from potentiometric titration data obtained with the glass and calomel electrodes.

Nickel and cobalt are very similar in their chemical behavior. Yet, it is obvious that the solution properties of their *o*-nitrosonaphthol salts must be fundamentally different in order for them to be useful in making an analytical separation. The compositions of the reaction products of cobalt and the *o*-nitrosonaphthols have been the subject of a considerable difference of opinion[5,6].

The present equilibria studies were undertaken with the expectation that the methods of coordination chemistry might shed some light on the nature of these complexes. Since the *o*-nitrosonaphthols are not specific for cobalt, a number of other metal salts of the ligands were investigated in order to provide sufficient equilibria data for comparing the various metal complexes. From the known analytical uses of the nitrosonaphthols it would be expected that differences should exist between the nickel and cobalt complexes.

EXPERIMENTAL

The pH measurements were made with a Beckman Model G pH meter using a Beckman Type E. No. 1190-80 glass electrode as the indicator electrode and a Beckman No. 1170 saturated calomel electrode as a reference electrode. The titrations were made at a constant temperature of 30.0° ± 0.1°C with nitrogen gas flowing first through an independent sample of the solvent at the same temperature and then over the solution being titrated. This solution was stirred continually except when making the actual pH measurement. The pH meter was calibrated against Beckman No. 14109 packaged buffer (pH = 4.01) at the beginning of each titration and with Beckman No. 14108 packaged buffer (pH = 9.14) when the pH of the titrated solution became alkaline.

Eastman White Label tetramethylammonium hydroxide (10% in water) was standardized and then diluted to furnish an approximately 0.1*N* titrating solution. No purification was attempted. Eastman Technical Grade 1-nitroso-2-naphthol was recrystallized from petroleum ether (m.p. 104-6°)[7] and stored in vacuum over BaO until used. Eastman White Label 2-nitroso-1-naphthol was recrystallized from glacial acetic acid (d. 160-5°) and stored in the same way as its isomer. Technical grade dioxan was refluxed with sodium for eight hours and then distilled. This procedure was repeated with the distillate and the final product was stored in dark bottles over Al_2O_3. Immediately before use the dioxan was run through a meter-long column packed with Linde Type 4A, 1/16 inch, molecular sieve pellets in an atmosphere of nitrogen. All bivalent-metal-ion solutions were prepared from G. Frederick Smith Chemical Co. Reagent Grade metal perchlorates. The tervalent-metal-ion solutions were prepared by dissolving the pure metal or the oxide of the metal in perchloric acid[8]. The stock solutions were standardized by standard analytical procedures. Pure dioxan solutions of the ligands were prepared by exactly weighing out the requisite amount of the ligand and dissolving in the required volume of dioxan. Potentiometric titrations of the ligand solutions using $(CH_3)_4NOH$ as the titrant gave the theoretical amount of replaceable hydrogen. These solutions were exactly 0.0100*M* with respect to the ligands. The metal ion solutions were approximately 0.004*M* with respect to the metal.

The 75-volume-% dioxan-water solution containing the desired ligand and metal ion was prepared by pipetting 50 ml of the 0.01*M* ligand solution into the titration flask followed by 25 ml of dioxan and 25 ml of the desired 0.004*M* metal ion stock solution. This gave an approximate ratio of 5 ligand molecules to every metal ion present. The solutions were allowed to stand in the thermostat for 30 min before commencing the titration. The 50-volume-% dioxan-water titration mixtures were prepared in the same way except that 25 ml of distilled water was substituted for the 25 ml of dioxan.

The thermodynamic constants were obtained by the procedure of VAN UITERT *et al.*[3,4] except that simultaneous equations were solved[9] instead of plotting formation curves.

DISCUSSION

50-volume-% dioxan-water

Initial titrations of the *o*-nitrosonaphthols and Mg(II), Cd(II), Zn(II), Ni(II), Hg(II), Co(II), Pb(II), Cu(II) and Ag(I) were made in 50-volume-% dioxan-water solutions. The stability constants calculated from these titrations are given in Table I. Bivalent Hg, Co and Pb as well as univalent Ag gave precipitates immediately when mixed with 1-nitroso-2-naphthol or so early in the course of the titrations that the constants could not be calculated. Copper liberated protons so extensively that the pH of the solution was in the insensitive portion of the pH scale. With 2-nitroso-1-naphthol the formation constant for Ag(I) was evaluated (Table I) but the results with Hg, Co, Pb and Cu cations were similar to those for the 1-nitroso-2-naphthol complexes.

TABLE I

THERMODYNAMIC CONSTANTS FOR 1-NITROSO-2-NAPHTHOL (pK_D = 9.47) AND 2-NITROSO-1-NAPHTHOL (pK_D = 8.90)[a] IN THE SOLVENT 50-VOLUME-% DIOXAN-WATER

Ligand	*Metal*	*log K_1*	*log K_2*	*log K_3*
1-Nitroso-2-naphthol	Mg(II)	3.60	3.47	
	Cd(II)	6.18	5.20	
	Zn(II)	6.76	5.68	
	Ni(II)	8.69	8.26	6.10
2-Nitroso-1-naphthol	Cd(II)	5.46	4.75	
	Zn(II)	5.70	5.22	
	Ni(II)	9.62	8.88	5.12
	Ag(I)	5.46		

[a] The values in water for pK_D are 7.77 and 7.38, resp.[10]

A comparison of the acid dissociation constants of the *o*-nitrosonaphthols (Table I) shows the anion of 1-nitroso-2-naphthol to be the stronger base. As would be expected under these circumstances, the metal salts of 1-nitroso-2-naphthol were more stable than the corresponding metal salts of 2-nitroso-1-naphthol with the curious exception of the nickel salts. No explanation can be offered for this apparent anomaly as this effect was not observed in 75-volume-% dioxan-water solvent (Table II). Further it is interesting to note that only log K_1 and log K_2 show this anomalous reversal of expected stability. Log K_3 for the nickel complexes are of the expected relative stabilities.

TABLE II

THERMODYNAMIC CONSTANTS FOR 1-NITROSO-2-NAPHTHOL (pK_D = 11.62) AND 2-NITROSO-1-NAPHTHOL (pK_D = 11.14) IN THE SOLVENT 75-VOLUME-% DIOXAN-WATER

Ligand	*Metal*	*log K_1*	*log K_2*	*log K_3*
1-Nitroso-2-naphthol	Mg(II)	6.05	4.72	
	Mn(II)	7.52	6.25	
	Cd(II)	8.64	7.31	
	Zn(II)	9.32	7.70	
	Pb(II)	9.73	7.58	
	Ni(II)	10.75	10.54	6.80
	Co(II)	10.67	12.14	
	Cu(II)	12.52	10.85	
	Ag(I)	7.74		
	Pr(III)	9.04	8.02	6.79
	Y(III)	9.02	8.72	7.30
	Nd(III)	9.5	8.2	7.86
2-Nitroso-1-naphthol	Mg(II)	5.62	4.35	
	Mn(II)	6.78	5.42	
	Cd(II)	7.96	6.70	
	Zn(II)	8.40	7.02	
	Pb(II)	8.93	7.14	
	Ni(II)	10.07	9.33	5.98
	Cu(II)	11.70	10.01	
	Ag(I)	7.55		
	Pr(III)	8.48	7.3	6.36
	Nd(III)	8.51	7.6	7.05
	Y(III)	8.3	7.6	7.4

75-volume-% dioxan-water

In 75-volume-% dioxan-water the values for log K_1 of the 1-nitroso-2-naphthol metal salts (Table II) can be arranged in the stability sequence Cu>Ni>Co>Pb>Zn>Cd>Mn>Mg. This is identical with the MELLOR AND MALEY[11] order of stability (except for the position of Pb between Ni and Co) and IRVING AND WILLIAMS[12] have given reasons why one would not expect a constant order for elements not in the first long period of the periodic table. However, the stability sequence based on log K_2 values is anomalous because of the unusual stability of Co(II). Possible causes of this enhanced stability are discussed below. 2-Nitroso-1-naphthol salts would probably show this same effect but unfortunately, the formation constants for the *beta*-isomer with cobalt could not be computed due to the fact that negative values were obtained from the simultaneous equations. This phenomenon has been discussed by BLOCK AND McINTYRE[9], but they could not determine its cause or the significance of the negative sign.

Bryant[13] developed a method for determining the formation constants of strongly complexing cations by displacing a weaker complexing cation from its complex salt. Attempts to adapt this procedure to the present problem by displacing the less stable Cd(II) ion from its 2-nitroso-1-naphthol complex by titrating with a Co(II) solution was not successful because values for $n < 1.80$ could not be calculated. Similar attempts to displace the somewhat more stable Pb(II) from its complex also yielded data that were useless for computing stability constants of the cobalt complex.

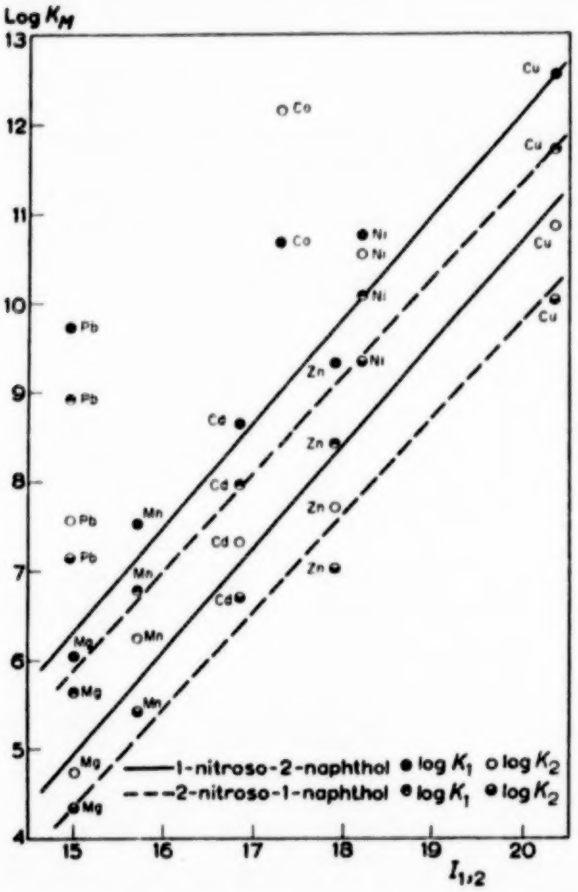


Fig. 1. Plot of log K_n of divalent metal nitrosonaphthol salts *vs.* the 2nd ionization potential, $I_{1,2}$ of gaseous atoms.

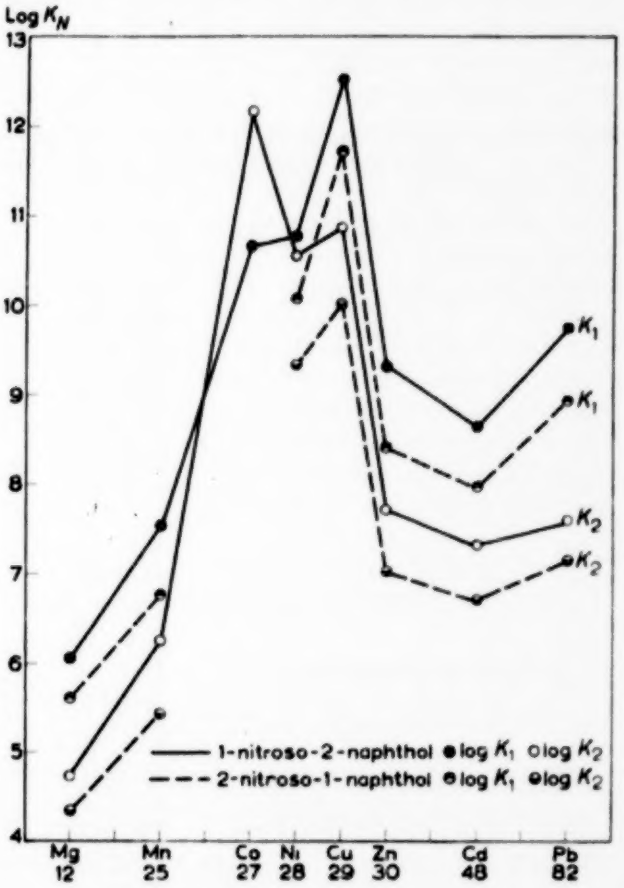


Fig. 2. Plot of log K_n of divalent metal nitrosonaphthols *vs.* atomic number.

Because of the strong complexing nature of copper and cobalt with 1-nitroso-2-naphthol it was necessary to combine the data obtained by titrating the metal-ligand mixture with $(CH_3)_4NOH$ with the data obtained by titrating the metal with a concentrated solution of the ligand. Attempts to secure constants for Hg(II), Fe(II), Fe(III), Al(III), Ga(III) and In(III) were unsuccessful. Only approximate values were obtained for Pr(III), Y(III) and Nd(III).

A number of attempts have been made to correlate the order of stability of complexes with the physical properties of the central metal ions. Irving and Williams[14] and Calvin and Melchior[15] independently reported a relationship between log K for a large number of complexes of the bivalent cations of the first transition series and their respective ionization potentials. Figure 1 shows such a plot for the nitrosonaphthols as measured in 75-volume-% dioxan-water solution. The log K_n of the formation constants are plotted against the second ionization potential, $I_{1,2}$, of the metal in the gaseous state. An approximate linear relationship is observed for log K_1 and both nitrosonaphthols with the significant exception of cobalt. Since lead is not included in this transition series, its log K value need not fall on the line. For the log K_2 values it is obvious that Ni(II) is also somewhat exceptional. However, only in the case of Co(II) is log $K_2 >$ log K_1. The IRVING-WILLIAMS correlation, log K_n *vs.* atomic number, is plotted in Figure 2. Again cobalt deviates from the expected behavior. Finally VAN UITERT[16] demonstrated the relationship between log K and X_M, the electronegativity of the metal ion. In Figure 3 the log K_n for the nitrosonaphthol salts are plotted against HASSINSKY's values of electronegativity[17]. Here again, essentially a linear relationship is observed with the exception of cobalt (and possibly nickel). In this plot lead also falls on the line.

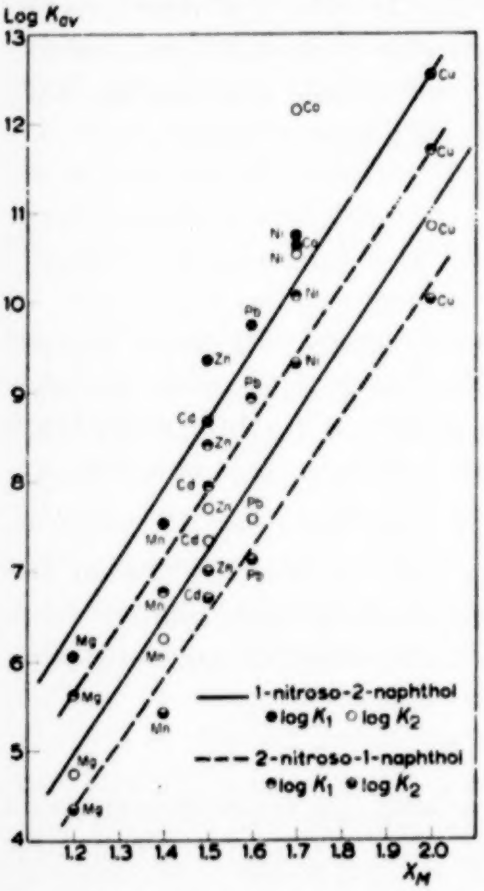


Fig. 3. Plot of log K_n of divalent metal nitrosonaphthol salts *vs.* electronegativity, X_M, of metal ion.

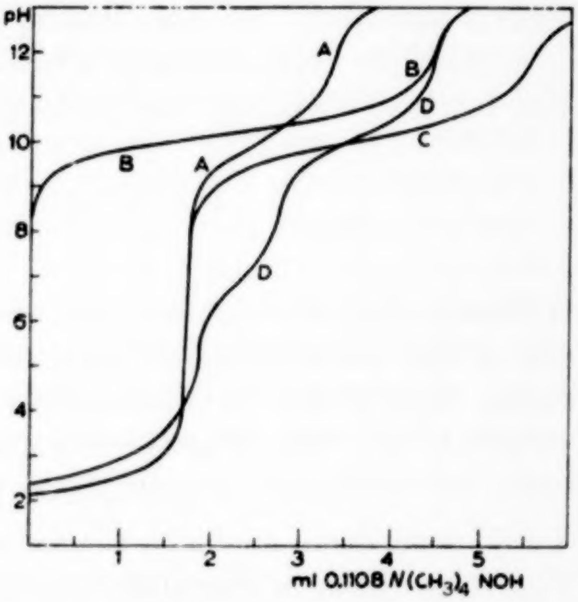


Fig. 4. Titration curve of Co(II) and Ni(II) and 1-nitroso-2-naphthol.

A. Titration curve of Co(II) and 1-nitroso-2-naphthol.

B. Titration curve of 1-nitroso-2-naphthol.

C. Titration curve of Co(II) and increased amount of 1-nitroso-2-naphthol.

D. Titration curve of Ni(II) and 1-nitroso-2-naphthol.

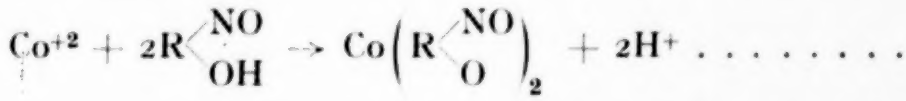
The cobalt salt of 1-nitroso-2-naphthol

1-Nitroso-2-naphthol was one of the first organic reagents which found application in qualitative and quantitative inorganic analysis[18] and has been the subject of a number of investigations[5,6,19–21]. The problems connected with the composition of the precipitate[19], amperometric titration[5], method of continuous variations[20], and reacting ratios[6,21] are reviewed in the reports on these investigations.

Data gathered during the present study of the stability of the cobalt nitrosonaphtholates may shed some light on this rather confusing situation. Calculations of the stability constants showed that only two ligands coordinated with cobalt. In Fig. 4, curve A is the titration curve from which the stability constants of the 1-nitroso-2-naphthol complex of cobalt was calculated. Approximately 5 molecules of ligand were present for every Co(II) ion. Curve B represents the titration of the same amount of

1-nitroso-2-naphthol as in curve A but without the cobalt. For curve A calculations show that two hydrogen ions are released by the coordination of two molecules of the ligand with each cobalt ion present. After these protons have been neutralized there is an abrupt rise in the pH from about 3 to 9. Then 1.75 molecules of excess uncoordinated ligand is titrated after which an inflection into more basic region indicates that all replaceable hydrogen has been neutralized. A total of 3.75 molecules of replaceable hydrogen has been accounted for, leaving 1.25 molecules to be accounted for. A check titration (Curve C) containing the cobalt to ligand ratio of 1 : 7.5 again left 1.25 molecules of protons or ligand unaccounted for. Thus PAULAIS' conclusion that 3.25 molecules are utilized in the coordination of Co(II) with 1-nitroso-2-naphthol[6] is confirmed. The same results were found with 2-nitroso-1-naphthol and cobalt.

A plausible explanation of what occurs is that divalent cobalt coordinates with two ligands, liberating two hydrogen ions for each cobalt ion present.



$$\mathrm{Co^{+2}} + 2\mathrm{R}\overset{\mathrm{NO}}{\underset{\mathrm{OH}}{<}} \rightarrow \mathrm{Co}\left(\mathrm{R}\overset{\mathrm{NO}}{\underset{\mathrm{O}}{<}}\right)_2 + 2\mathrm{H^+} \quad \ldots\ldots\ldots \quad (6)$$

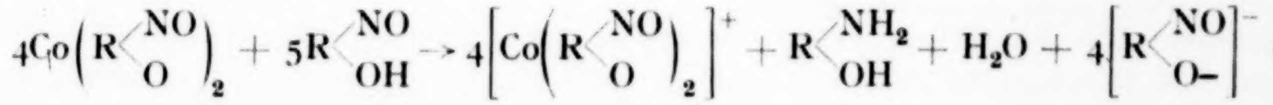
Although it is well known that coordination has a pronounced tendency to raise the oxidation potential of Co(II), it is assumed that the divalent complex is stable in the absence of heat and oxygen in the acid medium produced by the coordination process. The very low oxidation potential of divalent cobalt in acid solution

$$\mathrm{Co^{+2}} \rightleftarrows \mathrm{Co^{+3}} + e^- \qquad E^\circ_{298} = -1.84$$

would lend some credence to this assumption. At the end of the titration of the two equivalents of liberated hydrogen ions, the pH undergoes a large change from 3 to 9. In this change from an acidic medium to a basic medium the oxidation potential of divalent cobalt is raised to a very great degree.

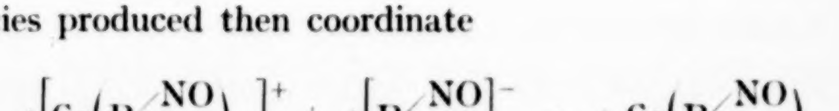
$$\mathrm{Co(OH)_2} + \mathrm{OH^-} \rightleftarrows \mathrm{Co(OH)_3} + e^- \qquad E^\circ_{298} = -0.20$$

In the change from the acid medium to the basic medium the quinone becomes a good oxidizing agent, so in the basic medium the bis(1-nitroso-2-naphtholato) cobalt(II) is easily oxidized to the tervalent state.



$$4\mathrm{Co}\left(\mathrm{R}\overset{\mathrm{NO}}{\underset{\mathrm{O}}{<}}\right)_2 + 5\mathrm{R}\overset{\mathrm{NO}}{\underset{\mathrm{OH}}{<}} \rightarrow 4\left[\mathrm{Co}\left(\mathrm{R}\overset{\mathrm{NO}}{\underset{\mathrm{O}}{<}}\right)_2\right]^+ + \mathrm{R}\overset{\mathrm{NH_2}}{\underset{\mathrm{OH}}{<}} + \mathrm{H_2O} + 4\left[\mathrm{R}\overset{\mathrm{NO}}{\underset{\mathrm{O-}}{<}}\right]^- \quad (7)$$

The ionic species produced then coordinate



$$4\left[\mathrm{Co}\left(\mathrm{R}\overset{\mathrm{NO}}{\underset{\mathrm{O}}{<}}\right)_2\right]^+ + 4\left[\mathrm{R}\overset{\mathrm{NO}}{\underset{\mathrm{O-}}{<}}\right]^- \rightarrow 4\,\mathrm{Co}\left(\mathrm{R}\overset{\mathrm{NO}}{\underset{\mathrm{O-}}{<}}\right)_3 \quad \ldots\ldots\ldots \quad (8)$$

to form tris(1-nitroso-2-naphtholato)cobalt(III). These reactions explain the disappearance of the 1 1/4 molecules of the ligand or what amounts to the same thing, the 1 1/4 hydrogen ions. One quarter of a molecule of the ligand is reduced to 1-amino-2-naphthol in the process of oxidizing Co(II) to Co(III). The dissociation of one molecule of ligand furnishes the necessary hydrogen for the reduction. The free naphtholate anion then combines with the complex cobaltic cation. Thus no record of the liberated hydrogen ions is observed in the titrations. This renders it impossible to calculate the log K_3 for the cobalt complex.

References p. 108

The analysis of the precipitate formed at the termination of the titration represented by curve C gave a cobalt to ligand ratio of 1 : 3 indicating that the tris complex was actually formed. On the other hand an analysis of the precipitate synthesized in a 50-volume-% dioxan-water solution gave a cobalt to ligand ratio of 1 : 2. The pH of this solution was acidic due to liberated protons attending the coordination. Thus the evidence indicates that the bis-complex exists in acid medium and is readily oxidized to the tris-complex in basic medium.

From the preceding discussion it may be inferred that 2-nitroso-1-naphthol is a better oxidizing agent than its isomer. The experimental results indicate that Co(II) is oxidized to Co(III) by this isomer in more acidic media than would be possible with 1-nitroso-2-naphthol. This would explain the failure to obtain stability constants with cobalt and 2-nitroso-1-naphthol. In this case the negative values obtained with the simultaneous equations would then indicate that the experimental data do not represent simple coordination equilibria, but represent a combination of coordination and oxidation-reduction equilibria. In other cases, hydrolysis or the formation of bridged compounds or of polymers might possibly also yield negative values.

The increased strength of the bonding of the second ligand to cobalt over that of the first is an unusual situation, since ordinarily each successive ligand is somewhat less firmly bonded than the preceding one. One possible explanation may be that the second ligand was added to tervalent cobalt rather than the bivalent cobalt, since log K_1 was calculated from data obtained by titrating Co(II) with the ligand and log K_2 was calculated from data obtained by titrating a mixture of the cobalt ion and excess ligand with standardized $(CH_3)_4NOH$.

Another explanation of this anomalous situation may be that the increased stability of the second ligand is due to orbital stabilization. Co(II) presents four possibilities in complex formation. It may form both tetrahedral ($4s4p^3$) and octahedral ($4s4p^34d^2$) "upper level" complexes in which there are three unpaired 3d electrons and square planar ($3d4s4p^2$) and octahedral ($3d^24s4p^3$) "lower level" complexes which contain only one unpaired electron[22,23]. On the assumption that the hydrated Co(II) is ionically ("upper level") bonded to four water molecules in the tetrahedral configuration, the first nitrosonaphthol adds to the cobalt with the retention of configuration. The second ligand could then add to the cobalt by utilizing additional "upper level" orbitals with retention of the tetrahedral configuration and the usual diminuation of bond strength, or by utilizing available "lower level" 3d orbitals with the consequent change to the square planar configuration and an increase of bond strength. The latter alternative would explain the increased stability of the second ligand over the first. The same line of reasoning could be used assuming that the hydrated Co(II) ion had the octahedral configuration. Utilization of "lower level" bonds would increase the bond strength of the attached ligands. The promotion of a lone 3d electron to 4d or 5s level would explain the ease of oxidation of the Co(II) complex to the Co(III) state. Analyses of the Co(II) and Co(III) complexes after drying at 150° indicated six coordination for both complexes. The Co(II) complex corresponded to $Co(C_{10}H_6NO_2)_2 \cdot 2H_2O$ and the Co(III) complex to $Co(C_{10}H_6NO_2)_3$.

Comparison of nickel and cobalt complexes

The value of the *o*-nitrosonaphthols as reagents for separating nickel from cobalt can now be explained. The stability constants (Tables I and II) and the titration curve D (Fig. 4) show that Ni(II) forms the tris-ionic species $Ni(C_{10}H_6NO_2)_3^-$. On the other hand Co(II) in the presence of the reagent in alkaline medium is oxidized to Co(III) by excess reagent and forms the neutral complex $Co(C_{10}H_6NO_2)_3$. The neutral cobalt complex is insoluble in mineral acids. On the other hand the ionic species of the nickel complex is soluble in mineral acids as would be expected.

ACKNOWLEDGEMENT

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SUMMARY

Formation constants of various metal derivatives of 1-nitroso-2-naphthol and 2-nitroso-1-naphthol have been measured in 50 and 75 volume per cent dioxan. The anomalies of the nickel and cobalt compounds are considered and explanations offered.

RÉSUMÉ

Les constantes de formation de plusieurs dérivés métalliques du 1-nitroso-2-naphtol et du 2-nitroso-1-naphtol ont été déterminées dans un milieu à 50 et 75 volumes pour cent de dioxane. Les anomalies des composés du nickel et du cobalt ont été examinées et des explications sont données.

ZUSAMMENFASSUNG

Die Bildungskonstanten verschiedener Metallderivate von 1-Nitroso-2-naphtol und 2-Nitroso-1-naphtol wurden in 50 und 75 volumprozentigem Dioxan bestimmt. Die Anomalien der Nickel- und Kobaltverbindungen wurden erörtert und Erklärungen hierfür gegeben.

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THE DETERMINATION OF URANIUM IN ALLOY SYSTEMS

by

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INTRODUCTION

The determination of the uranium content of certain uranium base binary and ternary alloys has been accomplished by a differential absorptiometric method[1]. Unfortunately this method is inapplicable to the analysis of alloys containing uranium as a minor alloying constituent because of the difficulty of obtaining a solution of the sample with a high enough uranium concentration. The most satisfactory method for determining milligram quantities of uranium so far investigated in this laboratory involves the reduction of the uranium to the tetravalent state by the passage of a hydrochloric acid solution of the sample through a lead reductor[2]. Then the reduced uranium is titrated with a standard ceric sulphate solution using ferroin as the indicator. BACON AND MILNER[3] found this technique valuable for the direct determination of the uranium content of aluminium-uranium binary alloys containing 20% of uranium. This is a very favourable alloy system, however, because the aluminium is not affected by the reduction process and, therefore, does not interfere in the ceric sulphate titration. Many elements can cause difficulty with the lead reductor, several are, for example, reduced to the metallic state and then cause blockage of the reductor. Bismuth belongs to this class of elements and one of our requirements included analysis of bismuth-uranium alloys containing uranium as a minor alloying constituent. Certain other elements are reduced to lower valency states by the lead reductor and then cause interference in the uranium determination by consuming some of the ceric sulphate solution. For a generally applicable method for the determination of uranium in alloy samples, therefore, some simple procedure for the separation of the uranium from other sample constituents is needed before the reduction of the uranium in the lead reductor.

According to the work of PŘIBIL AND VORLÍČEK[4], the separation of uranium can be obtained from many other elements by the precipitation of ammonium diuranate in the presence of ethylenediaminetetra-acetic acid (EDTA). However, we failed to achieve quantitative recoveries for uranium by this procedure. The precipitation of uranium with 8-hydroxyquinoline in the presence of EDTA has been used for the separation of this element from many other elements[5]. Such a separation procedure would, however, involve the destruction of organic matter before the passage of the uranium solution through the lead reductor. Attention was, therefore, directed to an investigation of inorganic precipitants. HURÉ, KREMER AND LE BERQUIER[6] have shown that beryllium can be separated from many elements by precipitating with ammonium phosphate at about pH 5 in the presence of EDTA. This method is based on the very weak complexation of beryllium with EDTA. Hexavalent uranium also forms a weak complex with EDTA and preliminary experiments showed that this element could be precipitated with diammonium phosphate in the presence of excess EDTA. After filtration and dissolution of this precipitate in hydrochloric acid, the reduction of the uranium by the lead reductor could be carried out without difficulty. This precipitation procedure appeared to offer a very simple method for separating the uranium from other alloying constituents forming stable complexes with EDTA under the conditions of precipitation. This method was, therefore, studied in some detail and is reported in this paper together with its application to the determination of uranium in bismuth-uranium alloys. Whilst this investigation was in progress, TILLU[7] independently reported on the possibility of separating uranium as its phosphate in the presence of EDTA. Very limited details are, however, given in his letter.

EXPERIMENTAL

In preliminary experiments solution conditions were quickly settled for the quantitative precipitation of the uranyl ammonium phosphate. The pH for precipitation was not critical and could readily be attained by first neutralizing the acidic sample solution with ammonium hydroxide to the alkaline colour of methyl red. Then an acetate buffer was added to produce the acid colour of the indicator, followed by diammonium phosphate to cause the precipitation of the uranium.

Although direct filtration could be employed for separating the phosphate precipitate after a suitable digestion period, a combination of centrifugation and filtration was found to be preferable because of the slow coagulation of the gelatinous precipitate. On re-solution of the precipitate in hydrochloric acid, the reduction and titration of the uranium was completed exactly as described in a previous paper[2]. Full details of the complete method for the uranium determination are as follows:

Procedure for the determination of uranium

Apparatus

M.S.E. major centrifuge with 250 ml centrifuge tubes. Lead reductor — take a burette of 10 mm internal diameter and insert a glass wool plug about 1" in length. Then add sieved lead powder (40-60 mesh) and tap the tube to assist the bedding down of the lead. Prepare a column about 30 cm in length and then insert a further pad of glass wool on the top of the column. Wash the column with 200 ml of $3N$ hydrochloric acid containing about 10 mg of ferric iron and then wash free from ferric iron with 200 ml of $1N$ hydrochloric acid. Keep the level of acid in the column at 2 or 3 cm above the top glass-wool plug and take precautions to keep air out.

Reagents

1. Approximately $0.02N$ ceric solution — dissolve 22 g of AnalaR ceric ammonium nitrate in 2 litres of N sulphuric acid. Standardize against arsenious oxide by transferring a 50 ml aliquot of a $0.0202N$ arsenious oxide solution with a calibrated pipette to a titration flask containing 20 ml of $10N$ sulphuric acid. Using the same pipette, transfer 50 ml of the ceric solution to the titration flask and then add 3 drops of $0.01M$ osmium tetroxide solution. Add exactly 1 ml of $0.001N$ ferroin and then complete the titration with the ceric solution to the discharge of the

pink colour, using a 5 ml semi-micro burette graduated in 0.01 ml. Carry out a blank titration also.

2. Uranyl chloride solution, 0.02*N* — freshly ignite a quantity of Specpure U_3O_8 and cool in a desiccator. Dissolve 1.4033 g of this material in a small quantity of (1 + 1) nitric acid and then evaporate the solution almost to dryness. Dissolve in hydrochloric acid and again evaporate almost to dryness. Repeat this process three or four times to remove nitric acid. Then dissolve the residue in 100 ml of 10% v/v hydrochloric acid and dilute to 1 litre with water in a graduated flask at room temperature.

3. Ferroin solution, 0.001*M* — dilute 4 ml of *o*-phenanthroline ferrous sulphate solution as supplied by Hopkins and Williams to 100 ml with distilled water.

4. Ethylenediaminetetra-acetic acid (EDTA), disodium salt, 10% w/v aqueous solution.

5. Other reagents were of analytical reagent grade.

Method

Take 150 to 200 ml of solution containing about 5-100 mg of uranium and add sufficient EDTA to complex other constituents and provide a small excess of this reagent. Add ammonium hydroxide dropwise with stirring to make the solution alkaline to methyl red. Then add sufficient of an acetate buffer 0.1*M* in acetic acid and in ammonium acetate to restore the acid colour of the indicator. Dissolve 2 g of diammonium phosphate in the solution and then heat to boiling. Boil for 2 to 3 minutes and digest hot for about 30 minutes. Transfer the solution to a 250 ml centrifuge tube, centrifuge for about 5 minutes and then pour the supernatant liquid through a Whatman No. 42 filter paper. Mix the precipitate in the centrifuge tube with a hot 2% w/v ammonium chloride solution containing a small amount of diammonium phosphate and re-centrifuge. Again pour the supernate through the filter paper. Repeat the washing and centrifuging of the precipitate in the centrifuge tube twice more and then wash the filter paper two or three times. Dissolve the precipitate in the centrifuge tube in hot 25% v/v hydrochloric acid and transfer it to the original precipitation beaker, using more of the hydrochloric acid for washing purposes. Open out the filter paper over the beaker, wash it with the hot 25% v/v hydrochloric acid and allow the washings to collect in the beaker. Dilute the solution to a volume of approximately 80 ml with 25% v/v hydrochloric acid, cool to room temperature and reserve for the reduction procedure.

Carry out blank determinations on the reductor column by passing 80 ml of a solution containing 20 ml of concentrated hydrochloric acid through the column at the rate of about 100 ml per minute. Wash the column with 80 ml of *N* hydrochloric acid added in small portions to obtain maximum washing efficiency. Transfer the solutions to a titration flask using *N* hydrochloric acid for washing purposes. Then add 2 ml of phosphoric acid (sp.gr. 1.75) and 1 ml of 0.001*N* ferroin and titrate with 0.02*N* ceric solution to the discharge of the indicator colour. Pass the uranium solution through the reductor, using 80 ml of *N* hydrochloric acid added in small portions to wash the beaker and the reductor column. Transfer the solutions to a titration flask using *N* hydrochloric acid for washing purposes. After adding 1 ml of 0.001*N* ferroin solution and 1 drop of phosphoric acid (sp.gr. 1.75) titrate rapidly with the standard ceric solution until the indicator colour just fades. Then add 2 ml of phosphoric acid and continue the titration slowly to the end-point. Correct this titre for the blank value and calculate the uranium content from the expression:

$$(x-B) \cdot 0.02 \cdot F \cdot 119.04^{*} \text{ mg uranium}$$

x = ml ceric solution used in the titration
B = ml ceric solution used in the blank titration
F = factor on normality of ceric sulphate solution.

RESULTS

Results for the recovery of uranium in the presence of EDTA

Recovery experiments were carried out for two levels of uranium both in the absence and in the presence of ethylenediaminetetra-acetic acid. A slight difference was observed in the nature of the precipitate produced in the presence of EDTA. It was less gelatinous than when precipitated in the absence of EDTA but even so the precipitate coagulated slowly and centrifugation could not be dispensed with. Essentially complete recovery of the uranium was obtained in all cases, indicating negligible interference from the presence of EDTA in solution at the precipitation stage. Details of the results obtained are given in Table I.

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* The equivalent weight of uranium will differ with its isotopic composition which should be known before any calculations are made. The equivalent weight of natural uranium is 119.04.

TABLE I

THE EFFECT OF EDTA ON THE URANIUM PRECIPITATION

No.	*Volume of 0.02N ceric solution for uranium determination*			*Remarks*
	Expected (ml)	*Obtained (ml)* *(1)*	*(2)*	
1	16.97	16.99	16.95	After phosphate precipitation
2	16.97	16.97	16.99	After phosphate precipitation in presence of 1 g EDTA
3	5.10	5.12	5.11	After phosphate precipitation
4	5.10	5.08	5.07	After phosphate precipitation in presence of 1 g EDTA

The effect of other elements

In experiments to test the uranium determination in the presence of other elements, solutions containing A.R. grade salts of these elements were added to measured aliquots of the standard uranium solution. Then sufficient of a 10% solution of the disodium salt of EDTA was mixed with the sample solution to complex the added constituent and provide a small excess of this reagent. The precipitation of the uranyl ammonium phosphate and the completion of the uranium determination was then carried out as described previously. This investigation was limited to elements of metallurgical interest, including iron, chromium, copper, nickel, vanadium, cerium, neodymium and bismuth. In the case of chromium it was found necessary to boil the solution for 10-15 minutes to obtain the complete formation of the EDTA complex. Table II shows some results obtained for two levels of uranium at different

TABLE II

THE EFFECT OF SOME ELEMENTS ON THE URANIUM DETERMINATION

Element	*Amount taken (mg)*	*EDTA taken (g)*	*Uranium taken (mg)*	*Uranium found (mg)*	*Difference (mg)*	*Remarks*
Iron	100	1	119.0	119.2	+0.2	
Iron	500	5	11.90	11.84	—0.06	
Chromium	100	1	119.0	118.9	—0.1	
Chromium	500	5	11.90	11.77	—0.13	
Copper	100	1	119.0	119.1	+0.1	
Copper	500	5	11.90	11.89	—0.01	
Nickel	100	1	119.0	118.8	—0.2	
Nickel	500	5	11.90	11.90	nil	
Vanadium	100	1	119.0	119.0	nil	
Vanadium	500	5	11.90	11.87	—0.03	
Cerium	30	1	11.90	11.92	+0.02	
Cerium	120	2	11.90	11.91	+0.01	Some cerium phosphate pptd.
Neodymium	30	1	11.90	11.86	—0.04	
Neodymium	120	2	11.90	11.91	+0.01	Some neodymium phosphate pptd.
Bismuth	2000	5	5.0	5.1	+0.1	
Bismuth	2000	5	10.0	9.98	—0.02	
Bismuth	2000	5	20.0	19.98	—0.02	

ratios of the elements. From these results the separation is very satisfactory even with fifty times as much of some elements, while at least four hundred times as much bismuth can be tolerated. No separation could be obtained by this procedure from stannic tin, stannous tin, molybdenum or tungsten. Tin formed a phosphate precipitate in the presence of EDTA. Molybdenum and tungsten on the other hand caused some delay in the precipitation of the uranyl ammonium phosphate. This delay could be offset by prolonged boiling of the solution, but after such treatment slightly high recoveries were obtained for uranium.

The determination of uranium in bismuth-uranium alloys

In testing the suitability of this procedure for the determination of the uranium content of bismuth-uranium binary alloys, weighed amounts of suitable alloys were dissolved in 25% v/v nitric acid. After the destruction of nitrites in solution with a small amount of urea, each solution was cooled and diluted to a convenient volume in a volumetric flask. Then suitable aliquots were taken for the determination of the uranium content of the sample. Several aliquots from two alloy solutions were analysed to obtain information on the reproducibility of the uranium determination. Results of 1.134 ± 0.009% and 1.800 ± 0.015% uranium respectively were obtained, the standard deviation in each case being calculated on seven results. In the complete analysis of alloy samples, further aliquots were taken for the determination of the bismuth contents by direct titration with EDTA using pyrocatechol violet as the indicator[8]. Results obtained in typical alloy analysis are reported in Table III.

TABLE III

RESULTS FOR BISMUTH-URANIUM ALLOYS

No.	*Nominal uranium content*	*Composition by analysis*		
		Bismuth (%)	*Uranium (%)*	*Total (%)*
1	10%	89.9	9.9	99.8
2	20%	80.0	20.3	100.3
3	4%	96.4	3.7	100.1
4	3.5%	96.6	3.5	100.1

Conclusion

The separation of uranium from many other elements by precipitation as uranyl ammonium phosphate in the presence of EDTA has been shown to be useful for the extension of the volumetric method for uranium in alloy analysis. This method is particularly suitable for alloys containing uranium as a minor alloying constituent and has been successfully applied to the analysis of bismuth-uranium alloys containing from approximately 1 to 20% of uranium. With this alloy system, the method should be applicable down to 0.5% of uranium.

SUMMARY

A procedure is described for the determination of the uranium content of metallurgical alloys containing this element as a minor constituent. The uranium is first separated from the sample solution by precipitation as uranyl ammonium phosphate in the presence of ethylenediaminetetra-acetic acid. By this means the uranium is separated from many elements including iron, chromium, copper, nickel, vanadium, cerium, neodymium and bismuth. The uranyl ammonium phosphate precipitate is dissolved in hydrochloric acid and the resulting solution is passed through a lead reductor. The tetravalent uranium is titrated with a standard ceric sulphate solution, using ferroin as the indicator. This procedure has proved very suitable for the analysis of bismuth-uranium binary alloys containing uranium in amounts up to approximately 20%.

RÉSUMÉ

Une méthode est décrite pour le dosage de l'uranium dans des alliages métallurgiques dont cet élément est un constituant secondaire. Il est d'abord séparé par précipitation comme phosphate d'uranyle et d'ammonium, en présence d'acide éthylènediamine-tétracétique. L'uranium peut être ainsi séparé de nombreux éléments, tels que le fer, le chrome, le cuivre, le nickel, le vanadium, le cérium, le néodyme et le bismuth. Le phosphate d'ammonium et d'uranyle précipité est dissous dans l'acide chlorhydrique et passé ensuite à travers un réducteur au plomb. L'uranium(IV) formé est titré au moyen d'une solution étalon de sulfate de cérium(IV), en présence de ferroïne comme indicateur. Cette méthode convient très bien aux alliages binaires bismuth-uranium, où l'uranium se trouve à des concentrations allant jusqu'à 20% environ.

ZUSAMMENFASSUNG

Ein Verfahren zur Bestimmung des Urangehaltes von metallurgischen Legierungen, welche das Metall als Nebenbestandteil enthalten, wird beschrieben. Das Uran wird erst durch Fällung als Uranylammoniumphosphat in Gegenwart von Äthylendiamintetraessigsäure aus der Lösung der Probe ausgeschieden. Auf diese Weise wird das Uran von vielen Elementen mit Inbegriff von Eisen, Chrom, Kupfer, Nickel, Vanadin, Cer, Neodym und Wismuth getrennt. Das gefällte Uranylammoniumphosphat wird in Salzsäure gelöst und die erhaltene Lösung durch einen Bleireduktor geführt. Das vierwertige Uran wird mit einer Titerlösung von Cer(IV)-sulphat in Gegenwart von Ferroin als Indikator titriert. Dieses Verfahren hat sich zur Analyse von binären Wismuth-Uran-Legierungen, welche bis zu ungefähr 20% Uran enthalten, als sehr geeignet erwiesen.

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THORIUM COMPLEX OF 2,7-DINITROSO-1,8-DIHYDROXYNAPHTHALENE-3,6-DISULPHONIC ACID

III. COMPLEXOMETRIC DETERMINATION OF THORIUM WITH ETHYLENEDIAMINETETRAACETIC ACID

by

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In recent years a number of analytical methods for the determination of certain cations, based on the formation of their complexes with chelating agents, have been reported in the literature.

The thorium complex of 2,7-dinitroso-1,8-dihydroxynaphthalene-3,6-disulphonic acid (dinitrosochromotropic acid) prepared earlier[1] has now been utilized in the direct titration of thorium with ethylenediaminetetraacetic acid (EDTA). The pinkish-violet thorium complex in acid medium is less stable than the colourless thorium-EDTA complex ($\log K = 23.2$). The method of titration consists of adding a standard solution of the di-sodium salt of EDTA to a flask containing an unknown amount of thorium nitrate and with dinitrosochromotropic acid as indicator. Thorium forms the complex with the indicator at once. When a considerable quantity of thorium has reacted with EDTA, the highly coloured thorium complex breaks down owing to the formation of a stronger complex of thorium with EDTA, marking the end of the titration. The colour change, from pinkish-violet to red, is very sharp at the end-point.

This process of titration is rapid and accurate; very small quantities of thorium may be determined by this method. The thorium complex of EDTA is very stable and moderate quantities of some foreign ions do not interfere. The results of titration using this reagent agree well with those obtained by xylenol orange indicator.

EXPERIMENTAL

Reagents and chemicals

Indicator solutions. These were a 0.025% solution of dinitrosochromotropic acid in water and a 0.02% solution of xylenol orange indicator also in water.

Thorium nitrate solution. A stock solution of thorium was prepared by dissolving the requisite quantity of thorium nitrate tetrahydrate (Merck's A.R.) in one litre of water. The thorium content of this solution was determined gravimetrically with 2:4-dichlorophenoxyacetic acid[2].

Solution of the di-sodium salt of ethylenediaminetetraacetic acid

The di-sodium salt of ethylenediaminetetraacetic acid (Merck's A.R.) dried over conc. H_2SO_4, was dissolved in distilled water to give a solution of the titrant (0.012*M*). This was standardized by standard $CaCO_3$ solution using murexide indicator[3].

Metal solutions. Stock solutions of salts of various metals (reagent grade) were prepared by dissolving the nitrates, chlorides or sulphates in water and were estimated by standard methods.

Optimum conditions for the determination of thorium

Concentration of the indicator

The colour change at the end-point is from pinkish-violet to red and the end-point colour should be matched with a blank. In order to test whether the concentration of the indicator solution has any effect on the titre value, titrations were carried out with different amounts of indicator solutions of varied concentration in 50 ml volume. It was seen that although the titre value was not appreciably affected by the amount or concentration of the reagent, the best results, *i.e.* giving sharp end-points, were obtained with 2 ml of 0.025% solution of the indicator per 50 ml volume.

Effect of dilution

The colour of the thorium complex and of the solution at the end-point, after the complex has been broken down by the action of EDTA, becomes so faint in too dilute solution that it is difficult to determine the end-point of the titration. Titrations were carried out varying the volume of the final titrating solution without changing the amount or concentration of the indicator. It was observed that dilution beyond 75 ml did not present a detectable end-point.

Effect of temperature

Titration of the thorium solution should be carried out at room temperature; a slight turbidity occurs if the mixture is heated beyond 60°.

Effect of pH

In order to discover a suitable pH range for the effective titrimetric determination of thorium, titrations were carried out in solutions with different pH values. The pH was adjusted by adding acetate buffer mixtures. The results recorded in Table I indicate that with dinitrosochromotropic acid the optimum pH range for the quantitative titration of thorium by EDTA is from 2.2 to 3.5. At high acidity the thorium-dinitrosochromotropic acid lake is extremely unstable.

TABLE I

EFFECT OF pH IN THE TITRATION OF THORIUM WITH EDTA

Thorium taken = 33.1 mg

pH	1.6	1.9	2.1	3	3.4	4.2
0.012*M* EDTA, ml	5.02	7.63	11.62	11.95	11.92	12.15
Th found (mg)	14.0	21.3	32.7	33.4	33.3	34.9

Stoichiometry

Aliquot quantities of standard thorium nitrate solution were titrated with EDTA in order to find out whether the method was stoichiometric for thorium. From the results of titrations recorded in Table II, it appears that the method is stoichiometric within the limits of experimental error.

Titrimetric procedure for pure thorium solution

A definite quantity of thorium nitrate solution was taken in a 250 ml Erlenmeyer flask, the pH of the solution was adjusted to 2.5, 2 ml of the dinitrosochromotropic acid indicator solution were added to it, and the mixture was finally diluted to 50 ml. The sample was then titrated with standard EDTA solution run in from a burette with constant agitation of the flask until the colour of the solution changed from pinkish-violet to red. The amount of thorium present in solution was determined as:

$$\text{g of Th} = 0.2321 \cdot V \cdot M, \text{ where, } V = \text{volume of EDTA solution and } M = \text{its molarity.}$$

With a view to obtaining a better end-point, the titration was continued slightly beyond the end-point and the excess EDTA was then back titrated with a standard thorium solution to the end-point with colour change in the reverse direction. As the colour change was now from red to pinkish-violet, the end-point was more distinct and this gave better results. A blank was also prepared for comparison purposes. From the total thorium present and the amount of excess thorium added during the back titration, the amount of thorium originally taken could be determined as:

$$\text{g of Th found} = \text{Th}_{\text{total}} - 0.2321 \cdot V_1 \cdot M_1,$$

where, V_1 = ml and M_1 = molarity of the standard thorium solution.

Typical results are shown in Table II.

In order to compare the results and examine the suitability of the method, similar titrations of thorium solution were carried out with EDTA solution at pH 2.3, using xylenol orange indicator. Here the end-point was the colour change from pinkish-violet to orange, and it was sharper than that with dinitrosochromotropic acid indicator. Back titration and comparison with a blank are not necessary when xylenol orange indicator is used. The results recorded in Table II, however, agree fairly well with those in Table III.

TABLE II

TITRATION OF THORIUM WITH EDTA USING DINITROSOCHROMOTROPIC ACID

Th taken g	*Standard EDTA soln. (0.012M) added* ml	*Excess standard EDTA soln. added beyond end-point* ml	*Standard Th(NO$_3$)$_4$ (0.0162M) added to get final end-point* ml	*Th found* g	*Difference* mg
0.0496	17.5	0.6	0.3	0.0494	−0.2
0.0331	11.9	0.5	0.3	0.0334	+0.3
0.0331	11.9	0.4	0.3	0.0332	+0.1
0.0331	12.0	0.5	0.4	0.0334	+0.3
0.0248	8.9	0.4	0.2	0.0252	+0.4
0.0248	8.8	0.5	0.2	0.0252	+0.4
0.0248	9.0	0.6	0.4	0.0253	+0.5
0.0124	4.4	0.3	0.2	0.0124	±0.0
0.0186	6.9	0.3	0.3	0.0189	+0.3
0.0093	3.4	0.2	0.15	0.0095	+0.2
0.0062	2.3	0.2	0.2	0.0063	+0.1
0.0031	1.2	0.2	0.15	0.0034	+0.3

TABLE III

TITRATION OF THORIUM WITH EDTA USING XYLENOL ORANGE

Thorium taken g	*Standard EDTA soln. added* ml	*Thorium found* g	*Difference* mg
0.0331	11.85	0.0331	±0.0
0.0331	11.83	0.0330	−0.1
0.0331	11.85	0.0331	±0.0
0.0248	8.90	0.0248	±0.0
0.0248	8.80	0.0246	−0.2
0.0248	8.80	0.0246	−0.2
0.0124	4.50	0.0126	+0.2
0.0124	4.40	0.0123	−0.1
0.0124	4.40	0.0123	−0.1

Effect of diverse ions on the determination of thorium

Interferences by foreign cations are manifested in their formation of stable EDTA complexes or of coloured or insoluble metal complexes with the indicator. The effects of a large number of ions have been studied. It was found that the following metals did not interefere: lithium, potassium, sodium, mercury(II), cadmium, calcium, barium, strontium, magnesium, aluminium, iron(II), cobalt, chromium, zinc, *etc.* Serious interference was caused by iron(III), cerium(III) and (IV), zirconium, lead, titanium, molybdenum, vanadium and gold. Interference by iron is quantitative. Uranium causes slight interference when present in smaller amounts. No interference was observed with the following anions: nitrate, chloride, sulphate, bromide, acetate, but those that interfere seriously are: phosphate, fluoride, molybdate, vanadate, citrate, oxalate and tartarate. Known amounts of thorium were titrated in the presence of equal molar amounts of various cations and anions; the results are given in Table IV.

TABLE IV

STUDY OF INTERFERENCES IN THE TITRATION OF THORIUM

Th taken = 33.1 mg

Ion added	*Materials*	*Standard EDTA soln. (0.012M)*		*Ion added*	*Materials*	*Standard EDTA soln. (0.012M)*	
		added ml	*theor. ml*			*added ml*	*theor. ml*
Na^+	Sodium nitrate	11.83	11.85	K^+	Potassium sulphate	11.84	11.85
Li^+	Lithium nitrate	11.85	11.85	NH_4^+	Ammonium nitrate	11.86	11.85
Ag^+	Silver nitrate		interferes	Cu^{+2}	Copper sulphate		interferes
Pb^{+2}	Lead nitrate		interferes	Cd^{+2}	Cadmium chloride	11.87	11.85
Hg^{+2}	Mercuric chloride	11.84	11.85	Sn^{+2}	Stannous chloride		interferes
Ca^{+2}	Calcium chloride	11.83	11.85	Ba^{+2}	Barium chloride	11.82	11.85
Sr^{+2}	Strontium nitrate	11.87	11.85	Al^{+3}	Aluminium sulphate	11.82	11.85
Cr^{+3}	Chromium sulphate	11.82	11.85	Ce^{+3}	Cerium nitrate		interferes
Mg^{+2}	Magnesium sulphate	11.87	11.85	Zn^{+2}	Zinc sulphate	11.86	11.85
Ni^{+2}	Nickel sulphate		interferes	Co^{+2}	Cobalt chloride	11.89	11.85
Sb^{+3}	Antimony chloride		interferes	Bi^{+3}	Bismuth oxynitrate		interferes
Mn^{+2}	Manganese sulphate	11.82		Ti^{+4}	Titanium sulphate		interferes
V^{+2}	Vanadium chloride		interferes	Zr^{+4}	Zirconium nitrate		interferes
Ce^{+4}	Ceric sulphate		interferes	UO_2^{+2}	Uranium nitrate		interferes
VO_3^-	Sodium vanadate		interferes	F^-	Sodium fluoride		interferes
Ac^-	Sodium acetate	11.88	11.85	Citr.$^-$	Sodium citrate		interferes
Oxal.$^{-2}$	Sodium oxalate		interferes	Tart.$^{-2}$	Sodium tartarate		interferes

Interference by iron and its elimination

Iron(III) interferes in two ways in the process of the titrimetric determination of thorium with EDTA. It forms a very strong EDTA complex ($\log K = 23.4$)[3] and with the indicator, dinitrosochromotropic acid, it also gives a dirty greenish-yellow colour. But iron(II) does not produce any coloration with the indicator and forms a comparatively weak complex with EDTA ($\log K = 14.2$). Hence thorium can be titrated with EDTA without any difficulty. The interference of iron(III) may be eliminated by careful reduction before carrying out the titration. In the presence of ascorbic acid, the interference of iron(III) can be entirely removed[4]. Accordingly, titration of thorium in the presence of various amounts of iron(III) was carried out in the presence of ascorbic acid, following the same procedure; the results given in Table V reveal that in the presence of ascorbic acid a large amount of iron(III) can be tolerated in the titration of thorium with EDTA.

References p. 120

TABLE V

Th taken mg	*Fe(III) added* mg	*Th-Fe ratio (approx.)*	*Ascorbic acid added* g	*Th found* mg	*Diff.* mg
12.4	12.8	1:1	0.5	12.2	—0.2
12.4	25.6	1:2	0.5	12.7	+0.3
12.4	51.2	1:4	1.0	12.6	+0.2
12.4	76.8	1:6	1.2	12.8	+0.4
12.4	102.4	1:8	1.5	12.7	+0.3

Separation of thorium from other interfering ions and subsequent determination with EDTA

Interfering metals like copper, lead, tin, rare earths, uranium, gold, titanium, *etc.*, if present in the thorium solution, may be removed by precipitating thorium from hot solution with *o*-anisilic acid (phthalanilic acid prepared from *o*-anisidine) at pH 3.6 adjusted with acetate buffer[5].

The precipitate was filtered, washed with hot water and then dissolved in a small amount of *N* HCl, the pH of the solution was adjusted and thorium was reprecipitated with an excess of the same reagent.

After a thorough washing the precipitate was dissolved in the minimum volume of HCl (1:1) boiled for 5 minutes and diluted to 50 ml, the pH having been adjusted to 2.5. Titration of thorium in this solution was carried out as before. But zirconium could not be removed by this process. Some of the results are shown in Table VI.

TABLE VI

REMOVAL OF INTERFERING METALS FROM THORIUM SOLUTION

Metals taken	*Amount* g	*No. of determinations*	*Th found* g	*Difference* mg
Th	0.0186	2	0.0183	—0.3
Cu	0.0115			
Th	0.0186	2	0.0182	—0.4
Pb	0.0216			
Th	0.0186	3	0.0183	—0.3
Sn(II)	0.0103			
Th	0.0186	3	0.0187	+0.1
Ce(II)	0.0327			
Th	0.0124	2	0.0122	—0.2
La	0.0139			
Th	0.0124	2	0.0121	—0.3
Ni	0.0207			
Th	0.0124	3	0.0128	+0.4
Bi	0.0312			
Th	0.0124	4	0.0122	—0.2
Ti	0.0413			
Th	0.0186	4	0.0183	—0.3
Au	0.0112			
Th	0.0186	4	0.0183	—0.3
U	0.0179			
Th	0.0186	3	0.0189	+0.3
V	0.0203			

DISCUSSION

The end-point in the titration is the colour change from pinkish-violet to red. The reverse end-point is more distinct than the direct one, and thus back titration, with a standard thorium nitrate solution (after addition of excess EDTA solution) is preferable. The results of this titration are comparable to those obtained with xylenol orange indicator, one of the most successful indicators for thorium. Because EDTA forms complexes with many metals, a number of interferences is also expected in the determination of thorium. But the large variety of both cations and anions that can be tolerated in the determination is remarkable. Although iron(III) reacts with both EDTA and the indicator, it can be efficiently masked with ascorbic acid prior to titration. The disadvantage of this titrimetric process is that thorium cannot be determined in the presence of the cerite earths, using this indicator. Anions such as phosphate, fluoride, citrate, tartarate, which react with thorium, also interfere. Highly coloured ions such as UO_2^{+2} interfere and for such coloured solutions, a photometric titration is applicable.

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SUMMARY

Thorium forms a pinkish-violet coloured complex with dinitrosochromotropic acid, which has been used as an indicator in the titrimetric determination of thorium with EDTA. The method is based on the fact that this coloured complex is less stable than the thorium-EDTA complex and breaks down after a bulk of thorium has reacted with EDTA; this marks the end-point, which is the change from pinkish-violet to red. As little as 3.1 mg of thorium present in 50 ml volume of solution may be accurately determined within a pH range from 2.2 to 3.5. The study of interferences revealed that quite a number of elements do not interfere; iron may be masked with ascorbic acid. Thorium may be determined by the same method, after separating it from many interfering ions by precipitating it with *o*-anisilic acid.

RÉSUMÉ

Le thorium forme un complexe violet rose avec l'acide dinitrosochromotropique, qui peut être utilisé comme indicateur pour le dosage volumétrique du thorium avec l'acide éthylènediaminetétraacétique. Cette méthode est basée sur le fait que ce complexe coloré est moins stable que le complexe thorium-acide éthylènediaminetétraacétique; au point final il y a virage du violet rose au rouge. On peut doser avec précision jusqu'à 3.1 mg de thorium dans 50 ml de solution à un pH allant de 2.2 à 3.5. Une étude de la spécificité montre que de nombreux éléments ne gênent pas; le fer peut être masqué par l'acide ascorbique. Le thorium peut être dosé par cette méthode, après précipitation au moyen de l'acide *o*-anisilique, pour le séparer de nombreux ions gênants.

ZUSAMMENFASSUNG

Das Thorium bildet mit der Dinitrosochromotropsäure eine rosa-violette Komplexverbindung, welche als Indikator bei der titrimetrischen Bestimmung von Thorium mit Äthylendiamintetraessigsäure verwendet wurde. Die Methode gründet sich darauf, dass diese Komplexverbindung weniger stabil ist als der Thorium-Äthylendiamintetraessigsäure-Komplex und am Endpunkt zerlegt wird; hierbei schlägt die Farbe der Lösung von rosa-violett in rot um. 3.1 mg Thorium in 50 ml Lösung können auf diese Weise bei pH 2.2-3.5 genau bestimmt werden. Viele Elemente stören die Bestimmung nicht; Eisen kann mit Ascorbinsäure maskiert werden. Das Thorium kann mit Hilfe dieser Methode, nach Trennung von vielen störenden Ionen durch Fällung mit *o*-Anisilsäure, bestimmt werden.

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INORGANIC ANALYSIS IN ORGANIC SOLVENTS
II. 8-HYDROXYQUINALDINE AS A REAGENT FOR THE DETERMINATION OF COPPER

by

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INTRODUCTION

8-Hydroxyquinaldine has been found to be suitable for the gravimetric determination of macro amounts of copper in pure cupric solutions, as the following results show: 0.1092 g of pure copper foil was dissolved in acid and precipitated with 8-hydroxyquinaldine. 0.6514 g of $Cu(C_{10}H_8ON)_2$ was obtained on drying the precipitate at 120°C, corresponding to precipitation of 99.8% of the original copper. Copper 8-hydroxyquinaldate forms a brown, crystalline precipitate of $Cu(C_{10}H_8ON)_2 \cdot 2H_2O$[1]; precipitation is complete over the pH range 5-8. On drying at 110 to 150°C, the water of hydration is lost, and the complex becomes green. When dissolved in an organic solvent that has not been intensively dried, a yellow or brown solution is obtained depending on the concentration, because complete rehydration occurs. These solutions obey the Beer-Lambert law at the absorption maximum (400 mμ), as the results in Table I show. The solvent used was 1+1 benzene-chloroform.

TABLE I

Wt. of $Cu(C_{10}H_8ON)_2$ mg	*Vol. in which dissolved ml*	*Copper, mg/100 ml*	*Optical density, 400 mμ, 1 cm path-length*
2.266	25	1.516	1.12
1.968	25	1.317	0.956
1.394	25	0.933	0.680
1.372	50	0.459	0.343
0.507	50	0.169	0.133
0.298	50	0.0996	0.071
0.148	50	0.0495	0.038

On the micro scale, however, precipitation of copper with 8-hydroxyquinaldine is not quantitative. On attempted precipitation of 0.5 mg of copper in 100 ml with 8-hydroxyquinaldine, the precipitate took several minutes to appear at all, and the recovery was not quantitative. Various quantities of copper were precipitated in the presence of other ions, and from solutions containing high concentrations of inorganic salts. Presented in Table II are results for recovery of copper from approximately 100 ml of solution when various additions were made to the solution: the copper was determined spectrophotometrically at 400 mμ, after a chromatographic separation, by reference to a graph prepared from the results given in Table I. Clearly, precipitation is not quantitative on the micro scale under any of the conditions employed.

TABLE II

Copper taken mg	*Other ions added*	*Salts added*	*Subsequent treatment*	*Copper recovered %*
0.055	1 mg Fe^{+3}		Filtered hot after 30 min	40
0.140	,,		,,	36
0.281	,,		,,	72
0.395	,,		,,	76
0.505	,,		,,	86
0.562	,,		,,	90
0.675	,,		,,	90
0.055	,,		Filtered after standing overnight at room temperature	78
0.140	,,		,,	89
0.281	,,		,,	94
0.562	,,		,,	96
0.281	0.5 mg Fe^{+3} + 1 mg Pb^{+2}		Filtered when cold	94
0.281	,, + 1 mg Ni^{+2}		,,	92
0.281	,, + 1 mg Zn^{+2}		,,	74
0.281	,, + 1 mg Hg^{+2}		,,	39
0.140	1 mg Fe^{+3}	12 g Na_2SO_4	,,	54
0.281	,,	,,	,,	66
0.562	,,	,,	,,	96
0.140	,,	30 g NaCl	Filtered after standing at 40-50°C overnight	92
0.281	,,	,,	,,	96
0.562	,,	,,	,,	98

Copper may be completely removed from aqueous solution as its 8-hydroxyquinaldate by means of a triple extraction into chloroform, and this fact is employed in the present determination. 8-Hydroxyquinaldine is not a specific reagent for copper, but reacts with all metals other than the alkalies, alkaline earths and aluminium. The copper 8-hydroxyquinaldate can, however, be separated quantitatively chromatographically from nearly all the complexes that are extracted with it. The 8-hydroxyquinaldates of all metals other than chromium[2] are strongly adsorbed on activated alumina from 1+1 benzene-chloroform; chromium is not adsorbed at all and is completely removed by washing with this solvent mixture. Chromium is not completely extracted from aqueous solution at pH 5-8 as 8-hydroxyquinaldate, and when present only as a minor constituent, is not found at all in the extract. Consequently, a simultaneous determination of chromium and copper is not possible. Also, traces of chromium 8-hydroxyquinaldate are destroyed by the very small amount of hydrogen chloride produced during evaporation of the wet chloroform extract. There is no evidence for the decomposition of copper 8-hydroxyquinaldate from this cause.

By development of the chromatogram with a 0.5% solution of 8-hydroxyquinaldine in 1+1 benzene-chloroform, copper 8-hydroxyquinaldate alone is quantitatively eluted. Copper 8-hydroxyquinaldate is dehydrated when adsorbed on alumina, a green band being formed, but when developed with a solution of 8-hydroxyquinaldine, the band changes to brown in colour, and the complex elutes entirely as the dihydrate. No movement of the complexes of other metals, apart from iron, molybdenum and vanadium, occurs. Adsorption bands of iron, molybdenum, and most of all, vanadium, are spread into very wide zones during the development, and a partial elution occurs when more than certain amounts of these three metals are present. These tolerance limits are: iron 0.5 mg, molybdenum 0.2 mg, and vanadium 0.01 mg for a 12-15 cm column of activated alumina; the amount of copper adsorbed on the column should be between 0.01 and 0.5 mg. The concentrations of iron and molybdenum may be conveniently reduced, when necessary, by ether extraction from a hydrochloric acid solution prior to complex formation and extraction[3,4].

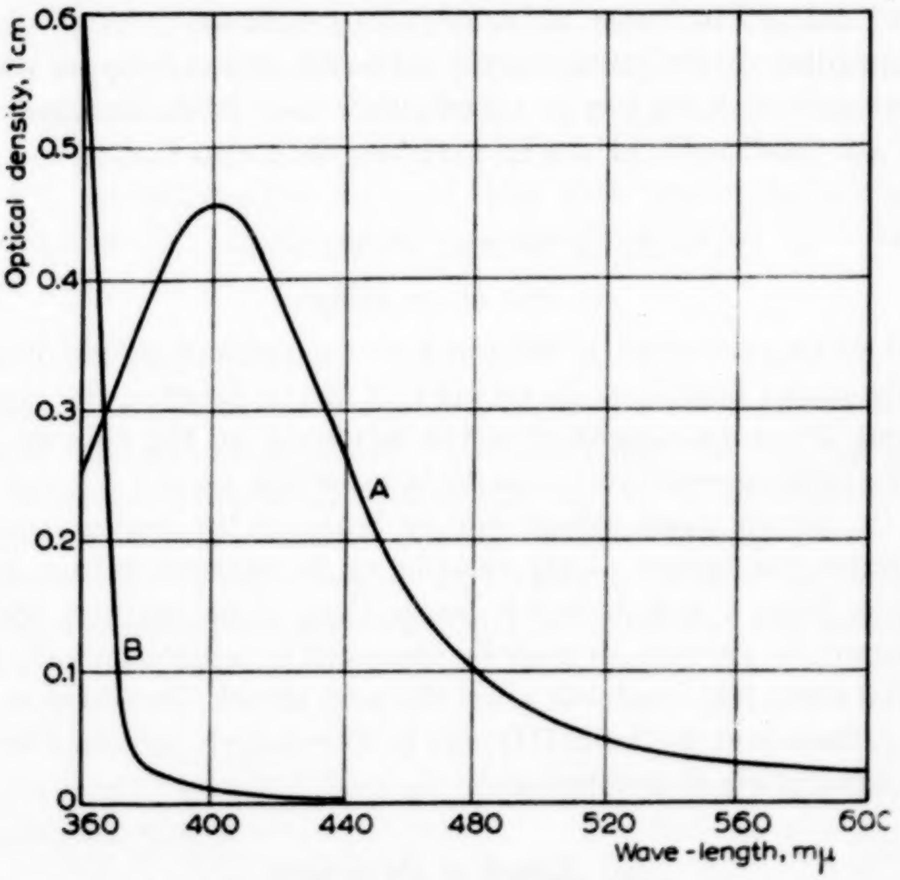

Fig. 1. Absorption curves of solutions of 8-hydroxyquinaldine and copper 8-hydroxyquinaldate in 1 + 1 benzene-chloroform. A. $10^{-4}M$ copper 8-hydroxyquinaldate, B. $2 \times 10^{-3}M$ 8-hydroxyquinaldine.

8-Hydroxyquinaldine does not absorb strongly above 380 mμ (see Fig. 1), but has a small, measurable absorption at 400 mμ. Because of this, a small blank must be subtracted from the optical density of the eluate containing the copper 8-hydroxyquinaldate, since a little of the 8-hydroxyquinaldine used to elute the copper appears in the eluate with it. If pure (colourless) 8-hydroxyquinaldine is used to prepare the eluting solvent, and the elution is carried out as described, and the eluate diluted to 50 ml, the blank optical density has a reproducible value of 0.007 ± 0.002 per cm path-length at 400 mμ. Although copper 8-hydroxyquinolate is similarly eluted from alumina by solutions of 8-hydroxyquinoline, 8-hydroxyquinaldine cannot be replaced by the more readily available 8-hydroxyquinoline in this determination, because 8-hydroxyquinoline reacts with the alumina of the column, forming aluminium 8-hydroxyquinolate, which elutes with the copper and causes a very serious interference.

Essentially this is a micro-method, but it is often necessary to take amounts of starting material which come into the macro range and to obtain the determination sample by taking a suitable aliquot of the aqueous solution of the sample; *e.g.*, to avoid sampling errors, and when a micro balance is not available. The method is applicable to the determination of copper in a wide range of materials, including alloys and ores of all kinds which do not contain appreciable amounts of vanadium. The copper may be determined with an accuracy of between 1 in 50 and 1 in 200 in most cases, depending on the nature of the material, and the copper content. Copper in amounts less than 0.15 mg per 50 ml of eluate may be determined with an accuracy of ± 0.5 μg, provided that a long path-length (4 cm) is used in the absorption measurements.

EXPERIMENTAL PROCEDURE

(i) Size of the sample

The amount of copper which is adsorbed on the column should be between 0.01 and 0.5 mg; the upper limit may be raised to 1 mg by diluting the eluate to 100 ml instead of 50 ml. The total weight of metals adsorbed on the column may be up to 5 mg, but iron, molybdenum and vanadium must not exceed 0.5, 0.2 and 0.01 mg respectively. In certain cases, where one or more of the major constituents may be removed during the attack of the sample, or by extraction into an organic solvent, the copper from a sample much larger than 5 mg may be adsorbed on the column. For example, aluminium may be dissolved in aqueous alkali, tin volatilised as bromide, and silica left insoluble after the acid attack. In addition, iron, molybdenum, gold, gallium and thallium(III) may be very largely removed by ether extraction from a hydrochloric acid solution.

(ii) Attack of the sample

General

Most copper-bearing materials require the use of nitric acid to dissolve the copper, but certain modifications are necessary with some types of alloys, as given below. Nitric acid must be removed by evaporation with sulphuric acid before addition of 8-hydroxyquinaldine because the reagent is readily oxidized by nitrate in dilute acid solution.

In cases where the iron, molybdenum, *etc.* concentrations are excessive, add an equal volume of hydrochloric acid to the diluted residue, and extract twice with an equal volume of ether. Boil off the ether from the aqueous layer and evaporate to expel most of the hydrochloric acid.

(a) Iron, nickel and chromium based alloys

These become passive in nitric acid and must be attacked initially with hot, dilute (1+3) sulphuric acid. If the attack is very slow (as when much nickel is present), add 10 ml of hydrochloric acid. When decomposition appears to be complete, add 10 ml of nitric acid and evaporate just to fuming.

(b) Non-ferrous alloys not attacked by aqueous alkalis, and low in tin and antimony

The majority of these alloys are completely attacked by nitric acid alone. Aqua regia should be used in the case of bullion too rich in gold to be attacked by nitric acid. When the attack is complete, add 5 ml of dilute (1+1) sulphuric acid and evaporate just to fuming. After dilution of the residue, add sufficient hydrochloric acid to precipitate any silver. Since hydrated stannic oxide adsorbs sufficient copper to invalidate the precision of the method, materials containing significant amounts of tin should be attacked by procedure (d).

(c) Aluminium and other alloys attacked by aqueous alkalis

If the alloy is rich in aluminium, zinc, or other metal which dissolves in alkalies, cover the sample with hot water and add 10% sodium hydroxide, a little at a time, until the metal is completely attacked. The sample-weight must be chosen according to the proportion of alkali-insoluble metals. Filter off the alkali-insoluble residue, wash it with 1% sodium hydroxide, and then with water. Attack the residue as described above, case (a), or (b), destroying the filter paper by evaporation with sulphuric-nitric acid mixture.

(d) Alloys rich in tin and antimony

To the sample add a mixture of 20 ml of hydrobromic acid, 2 ml of bromine, 0.5 ml of sulphuric acid, and evaporate slowly just to dryness. To the residue add a mixture of 20 ml of hydrobromic acid, 2 ml of bromine, 10 ml of dilute (1+1) sulphuric acid, and evaporate slowly, without boiling, just to fuming in an open beaker. Dilute the residue with 20 ml of water, and warm to dissolve all soluble salts. By this method, tin and antimony are volatilised as bromides, and lead remains insoluble as sulphate.

(e) Ores, minerals, etc.

Copper is completely extracted from all its ores, when finely ground, by digestion with concentrated nitric acid.

(iii) Extraction of copper 8-hydroxyquinaldate

If an aliquot is to be taken of the aqueous solution, it should be diluted in a standard flask to a volume such that a 10 ml aliquot will contain a convenient weight of copper. If the copper is to be extracted from the whole of the sample, not more than 2 ml of concentrated sulphuric acid should be used in the attack: after the final fuming, dilute the solution to 10 ml.

Lightly grease the stopcock and stopper of a 50 ml short-stemmed separating funnel with silicone lubricant, and place in it 10 ml of chloroform. Add the aqueous solution, or a 10 ml aliquot of it. Add 1 ml of 2% 8-hydroxyquinaldine in $2N$ acetic acid, followed by sufficient dilute (1+1) aqueous ammonia to produce a faint permanent precipitate; then add 5 ml of $4N$ ammonium acetate. Swirl gently, and, if necessary, adjust the pH to approximately 6 by addition of a few drops of dilute ammonia or sulphuric acid. Stopper the funnel and shake vigorously. Allow the layers to separate completely and run out the chloroform solution into a 100 ml beaker; add 2 ml of chloroform to the funnel, swirl, and run it out into the beaker. Add 10 ml of chloroform to the funnel, followed by 0.5 ml of the 8-hydroxyquinaldine solution; shake vigorously and allow the layers to separate. Draw off the chloroform layer into the same beaker and repeat the extraction, adding a further 10 ml of chloroform and 0.5 ml of the 8-hydroxyquinaldine solution. Add the third extract to the beaker containing the chloroform from the other two, taking great care in all cases not to let any of the aqueous solution pass into the beaker. Three extractions are invariably sufficient for the complete separation of copper.

(iv) Chromatographic separation and determination of copper

Evaporate the combined chloroform extract, containing the copper 8-hydroxyquinaldate, to 5-10 ml, and add an equal volume of benzene. If chromium is present in an amount greater than 0.05 mg, evaporate the chloroform extract rapidly just to dryness, and heat the residue in an oven at 130°C for up to two hours to sublime the excess 8-hydroxyquinaldine. Copper 8-hydroxyquinaldate is only weakly adsorbed on alumina in the presence of the amount of 8-hydroxyquinaldine present in the extract, and if this were not removed, some copper would be lost during the elution of the chromium. Dissolve the residue in 10 ml of 1+1 benzene-chloroform. If less than 0.05 mg of chromium was present in the aqueous solution from which the 8-hydroxyquinaldates were extracted, the procedure for its separation may be omitted.

Prepare a column of activated alumina 12-15 cm high in 1+1 benzene-chloroform as previously described[2]. Run out the solvent, leaving 1 cm above the alumina. Pour the solution of the 8-hydroxyquinaldates into the tube; wash the beaker twice with 2 ml of 1+1 benzene-chloroform, and add the washings to the tube. Open the stopcock fully, allowing the liquid to flow through; when all the solution has passed into the alumina, wash down the inside of the tube with 2 ml of 1+1 benzene-chloroform, and allow the washings to flow through. If chromium has to be removed, pass 25 ml of 1+1 benzene-chloroform through the column, rejecting the eluate. Develop the column with 25 ml of 0.5% 8-hydroxyquinaldine in 1+1 benzene-chloroform, with the stopcock fully open; collect the eluate in a dry 50 ml graduated flask. When all this solution, containing the copper, has passed through the column, wash it with 1+1 benzene-chloroform until the flask is full to the mark. Stopper the flask and mix the contents well. Measure the optical density of the solution at 400 mμ; the path-length should be chosen according to the colour-intensity of the solution.

Determine the blank to be subtracted from the optical density of the copper solution by passing 25 ml of the developing solvent through a clean alumina column, and diluting to 50 ml by washing the column with 1+1 benzene-chloroform.

(v) Standards

Prepare pure copper 8-hydroxyquinaldate by precipitating a dilute solution of an A.R. copper salt with a slight excess of 8-hydroxyquinaldine, and drying the precipitate at 120°C. Dissolve various weights of the precipitate in known volumes of 1+1 benzene-chloroform, and measure the optical densities of the solutions at 400 mμ. Plot a graph of optical density against copper concentration: this is a straight line as far as optical densities can be measured accurately.

DISCUSSION

(vi) Interferences and sources of error

To obtain accurate results, three conditions must be fulfilled:

(a) All the copper in the aqueous solution must be extracted as its 8-hydroxyquinaldate. This was found to be so when three extractions were made at pH 5-8, with further small additions of the reagent before the second and third.

(b) All the copper must appear in the eluate from the column and no elution must occur of the other metals adsorbed on it. All the copper will elute if the correct concentration of 8-hydroxyquinaldine is used as eluting solvent. Table III gives the percentage elution of 0.375 mg of copper from an alumina column by 25 ml of solutions of 8-hydroxyquinaldine of different concentrations in 1+1 benzene-chloroform.

Of the metals investigated, namely Fe^{III}, Al, U, Ce, Ti, Ni, Cr, Mo, Mn, Co, Th, Zn, V^{V}, W, Ga, In, Tl, Sn and Sb, it has been found that chromium, iron, molybdenum and vanadium lead to erroneous results by contributing to the absorption

TABLE III

Concentration of reagent, %:	1.00	0.50	0.25	0.10	0.05
Copper eluted, % :	100	100	97	93	82

of the eluate. No interference need be caused by chromium in any amount, because it can be completely eluted from the column before elution of the copper. Iron, molybdenum and vanadium partially elute with the copper when present in amounts greater than the stated tolerance limits. The concentrations of iron and molybdenum are readily reduced below these limits by ether extraction from a hydrochloric acid solution. The interference due to vanadium, however, for which the tolerance limit is very low, cannot be overcome except by a prior separation of copper as sulphide. Vanadium is extracted as its yellow 8-hydroxyquinaldate over the pH range 3-8: below pH 3, no extraction of copper occurs, and above pH 8, extraction of copper is incomplete. Addition of hydrogen peroxide or fluoride does not prevent the extraction of vanadium 8-hydroxyquinaldate over the pH range in which the extraction of copper 8-hydroxyquinaldate is quantitative.

(c) The blank to be subtracted from the optical density of the copper 8-hydroxyquinaldate solution to correct for the absorption of the 8-hydroxyquinaldine which passes through the column must have a definite, reproducible value. If pure, colourless, double steam-distilled 8-hydroxyquinaldine is used to prepare the eluting solvent, the blank has a constant value of 0.007 ± 0.002 per cm path-length. If the yellowish material, obtained by recrystallisation of the crude product, is used, variable blanks of up to twice the value quoted are obtained. Alternatively, the optical density of the copper solution can be measured against a blank, but by measurement against the solvent and subtraction of the correction stated above, the need for using an additional column with each group of determinations is eliminated.

(vii) Results

The results given in Table IV illustrate the wide range of materials and copper concentrations which can be analysed by this method.

The analytical results in Table IV are those of determinations on true replicates on the original sample. Agreement between replicates is seen to be very good in all instances, and the results close to those of analyses by classical methods, except in the case of materials containing vanadium.

TABLE IV

Material		*Approx. sample wt.* g	*Analytical results* %	*Mean* %	*Copper by standard methods* %	*Vanadium* %
Manganese brass	BCS 179	0.025	58.9, 58.8, 59.0	58.9	58.8	—
White metal	BCS 178	0.1	4.18, 4.19	4.18	4.08	—
White metal	BCS 177	1.0	0.316, 0.316	0.316	0.33	—
Carbon steel	BCS 218	0.5	0.172, 0.174	0.17	0.16	<0.003
Low alloy steel	BCS 253	0.2	0.655, 0.640	0.65	0.49	0.22
Alloy cast iron	BCS 173	0.05	5.14, 5.16	5.15	4.73	3.97
Aluminium alloy	BCS 181	0.1	4.68, 4.70	4.69	4.64	—
Cupriferous quartz		0.1	3.54, 3.50, 3.56	3.53	3.50	<0.01
Malachite		0.05	56.7, 56.5	56.6	56.0	<0.01
Chalcopyrite		0.05	33.9, 34.1, 33.9	34.0	34.2	<0.01

(viii) Notes on reagents and instruments

(a) Benzene and chloroform: the qualities of these solvents must be the same as those used in the chromatographic determination of chromium[2].

(b) 8-Hydroxyquinaldine: the commercial material is expensive and impure. This reagent was prepared by the method described by MERRITT AND WALKER[5], with the following modification: after steam distillation of the 8-hydroxyquinaldine from the reaction mixture, crush the product and leave exposed to the air for a week. Pure white 8-hydroxyquinaldine is then obtained by a second steam distillation. The only impurity in the crude product is *o*-aminophenol, which oxidizes to a non-volatile red solid on exposure to the air.

(c) Activated alumina: all the work described in this paper has been based on the Peter Spence product, Type H (100-200 mesh). This alumina requires no further activation before use, but must be stored in a tightly closed container. Its activity is between Brockmann Grades I and II[6].

(d) Spectrophotometer: the optical density measurements were made on a Unicam S.P. 600 Spectrophotometer.

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SUMMARY

A new method is described for the determination of copper. From a suitable solution, copper is extracted as its 8-hydroxyquinaldine complex into chloroform. The solution is diluted with an equal volume of benzene and passed through an activated alumina chromatographic column, whereupon all the 8-hydroxyquinaldates, except that of chromium, are adsorbed. Copper is eluted completely by developing the column with a 0.5% solution of 8-hydroxyquinaldine in that solvent mixture. The optical density of the eluate is measured at 400 mμ with respect to the solvent. Iron, molybdenum and vanadium interfere, but interference due to iron and molybdenum is readily overcome by a simple preliminary treatment.

RÉSUMÉ

Une nouvelle méthode est décrite pour le dosage du cuivre. A partir d'une solution adéquate, le cuivre est extrait sous forme de son complexe avec la 8-hydroxyquinaldine, dans le chloroforme. La solution obtenue est diluée avec un volume égal de benzène et passée à travers une colonne chromatographique d'alumine activée; tous les 8-hydroxyquinaldates sont adsorbés, à l'exception de celui de chrome. Le cuivre est ensuite élué totalement en développant la colonne avec une solution à 0.5% de 8-hydroxyquinaldine dans le mélange benzène-chloroforme. La densité optique de l'éluat est déterminée à 400 μm, par rapport au solvant. Le fer, le molybdène et le vanadium gênent, mais la perturbation causée par le fer et le molybdène peut être facilement évitée par un simple traitement préliminaire.

ZUSAMMENFASSUNG

Eine neue Methode zur Bestimmung von Kupfer wird beschrieben. Aus einer geeigneten Lösung wird das Kupfer als 8-Oxychinaldin-Komplex mit Chloroform extrahiert. Die Lösung wird mit einem gleichen Volumen Benzol verdünnt und durch eine chromatographische Säule von aktiviertem Aluminiumoxyd geleitet an welcher alle 8-Oxychinaldin-Verbindungen ausser der Chromverbindung, adsorbiert werden. Durch Entwickeln der Säule mit einer Lösung von 8-Oxychinaldin in demselben Lösungsmittelgemisch wird das Kupfer vollständig eluiert. Die optische Dichte des Eluates wird bei 400 mμ im Vergleich zum Lösungsmittel gemessen. Eisen, Molybdän und Vanadin stören, aber die Störung durch die beiden Erstgenannten kann mit Hilfe einer einfachen Vorbehandlung vermieden werden.

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THE THERMOLYSIS OF ZIRCONIUM PRECIPITATES

I. SALTS OF ORGANIC ACIDS

by

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INTRODUCTION

During the past few years a great amount of interest has been shown in the analytical chemistry of zirconium. Because of its occurrence with thorium and other Group IV elements, emphasis has also been placed on means of separation by forming insoluble zirconium compounds. Many of the insoluble compounds of zirconium used in the separation schemes have been useful in gravimetric procedures. A number of the precipitating agents form stoichiometric insoluble compounds with zirconium and can usually be weighed directly, providing they are sufficiently stable thermally. However, many of the insoluble precipitates are basic in nature and have variable compositions so that they have to be ignited to zirconium oxide.

The thermal stabilities of a large number of zirconium precipitates which are useful analytically have been studied by DUVAL[1]. The only precipitate containing organic material which could be weighed directly as precipitated was ziconium mandelate. The other precipitates containing organic compounds did not give stoichiometric compounds and were ignited to ZrO_2. The oxide levels were all reached in the 825° to 900°C range. With 8-quinolinol, the ZrO_2 level was not obtained even at 1011°C.

A number of new organic precipitants have been introduced since DUVAL's investigations. The new precipitates examined on the thermobalance in this study are the zirconium salts of phthalic[2], phenoxy-acetic[3], cinnamic[4], diphenic (2,2'-biphenyldicarboxylic)[5], *p*-bromomandelic[6], benzilic[7,8], *m*-cresoxyacetic[15], salicylic[3,9], and benzoic acids[10] and of 8-quinolinol[11]. All the precipitates have been previously prepared in the literature.

EXPERIMENTAL

Chemicals

Zirconyl chloride, C. p., was obtained from the Fairmount Chemical Co., Inc., Newark 5, N. J. (U.S.A.).

m-Cresoxyacetic acid was obtained from Purkis, Williams, Ltd., London, England.

p-Bromomandelic acid was obtained from Pilot Chemicals, Inc., Waltham, Mass. (U.S.A.).

All the other organic acids were obtained from Eastman Organic Chemicals, Rochester 3, N.Y. (U.S.A.).

All the other chemicals used were of reagent grade quality.

Thermobalance

The thermobalance used has been previously described[12]. The weight of the samples ranged from 100 to 150 mg. The heating rates on all samples were 4.5° per minute with a maximum temperature limit af about 900°.

Preparation of zirconium precipitates

The zirconium precipitates were prepared according to the procedures given by the original investigators[2-11]. All of the precipitates were dried at room temperature for at least 24 hours before pyrolysis on the thermobalance.

DISCUSSION

The thermal decomposition curves of the zirconium precipitates are shown in Figs. 1 and 2. In general, the precipitates exhibited varying degrees of thermal stability. The first weight loss occurred in the temperature range of 45° to 160°. After decomposition through various intermediates, the oxide (ZrO_2) levels were obtained from 500° to 790°. In all cases oxide levels were obtained 200 to 500° below the usual ignition temperature of 1000° recommended by many of the investigators. The minimum oxide level temperatures are recorded in Table I.

TABLE I

MINIMUM OXIDE LEVEL TEMPERATURES OF THE ZIRCONIUM PRECIPITATES

Precipitate	*Temperature**, °*C.*
Zirconium phthalate	525
Zirconium phenoxyacetate	565
Zirconium cinnamate	600
Zirconium diphenate	505
Zirconium 8-quinolinol	610
Zirconium *p*-bromomandelate	550
Zirconium benzilate	500
Zirconium *m*-cresoxyacetate	585
Zirconium salicylate	790
Zirconium benzoate	500

* Heating rate of 4.5° per minute.

Zirconium phthalate

Phthalic acid will precipitate zirconium from solutions 0.35*N* in HCl[2]. Since bivalent metal ions were not precipitated, this was described as an excellent method for the separation of zirconium. To separate zirconium from Ti, V and Cr, it was found that a double precipitation was required.

The thermal decomposition curve is shown in Fig. 1. The formula of the precipitate corresponded to $Zr[C_6H_4(COO)_2]_2$ with some contamination with basic salts. The precipitate was stable up to 80° where it began to decompose slowly. After various stages of decomposition and oxidation of the carbonaceous material, the oxide level was reached at 525°. There was no further change in weight even on extending the temperature to 900°. The possibility of weighing the stoichiometric normal zirconium salt was ruled out because of the variable composition of the precipitated compound as shown by the thermolysis curve.

Zirconium phenoxyacetate

Zirconium is precipitated with phenoxyacetic acid in 0.24*N* HCl solutions with the same degree of separation from other elements as was the case with salicylic acid[3]. The thermal decomposition curve is shown in Fig. 1. The formula of the precipitated salt corresponded to $ZrO(C_6H_5OCH_2COO)_2$. The curve was very similar to that for zirconium phthalate. The first weight loss occurred at 80° which after decomposition and oxidation of most of the carbonaceous material resulted in a horizontal beginning at 400°. Some carbonaceous matter was still present which was gradually oxidized to give the oxide level beginning at 565°.

Zirconium cinnamate

Cinnamic acid precipitates zirconium from boiling 0.1*N* acid solutions containing ammonium chloride. Good separations were obtained of zirconium from Th, Mn, U and cerite rare earths but not from Ti, V, Cr or Sn[4]. The thermal decomposition curve is shown in Fig. 1. The formula of the precipitated salt corresponded to $ZrO(C_6H_5C_2H_2COO)_2$, in disagreement with the previously reported composition of 1 ZrO_2 to 1 cinnamic acid. Obviously, the composition of the precipitate is variable depending upon the conditions of precipitation. The precipitate was stable up to 75° where it began to decompose slowly. After various stages of decomposition and oxidation the oxide level was obtained beginning at 600°. Previous investigators had ignited the precipitate to the oxide at an unspecified temperature.

Zirconium diphenate

Originally, diphenic acid was used to separate thorium from a number of other elements[5]. It was also found that zirconium could be effectively separated from thorium if the precipitation was carried out at a pH 2. Thorium was found to precipitate with this reagent if the pH increased to 4.5 to 8.6. The original investigators found that the zirconium salt was not stoichiometric and was ignited to the oxide at an unspecified temperature.

The thermal decomposition curve of zirconium diphenate is shown in Fig. 1. The formula for the compound can be represented as $Zr[(C_6H_4COO)_2]_2$ contaminated with some of the basic salt. The precipitate was stable up to 50° where it began to decompose slowly. Rapid oxidation of the organic material began at 400° resulting in the oxide level beginning at 505°.

Zirconium 8-quinolinol chelate

DUVAL[1] has previously studied the thermal decomposition of this precipitate and found that a horizontal corresponding to $Zr(C_9H_6NO)_4$ was not obtained. Instead, the decomposition curve descended all the way to 820° but the oxide level was not obtained even at 1011°. BALANESCU[13], who proposed the original method, suggested drying of the precipitate at 130° to 140°, and weighing the precipitate as $Zr(C_9H_6NO)_4$. BORREL AND PÂRIS[14] state that the precipitated compound does not correspond to any simple formula but may be considered a mixture of varying proportions of $ZrO(C_9H_6NO)_2$, $Zr(OH)_2(C_9H_6NO)_2$, $ZrO(OH)(C_9H_6NO)$ and $ZrO(OH)_2$.

The thermal decomposition curve of the 8-quinolinol chelate of zirconium is shown in Fig. 1. The formula of the precipitated chelate corresponded very closely to that of

$2\,ZrO_2 \cdot 3\,C_9H_7NO$. According to BALANESCU[13], the variability of composition of the precipitate from the normal chelate appears to be due to the degree of dispersion of the aggregates rather than to chemical causes. The precipitate began to lose weight at 45° but did not give a horizontal in the 100° to 200° range. Beyond 200° the precipitate began to decompose rapidly resulting in the oxide level beginning at 610°. The oxide level began at a a lower temperature than that given by DUVAL. From the results of this study it appears that the 8-quinolinol method should be abandoned as a gravimetric determination of zirconium.

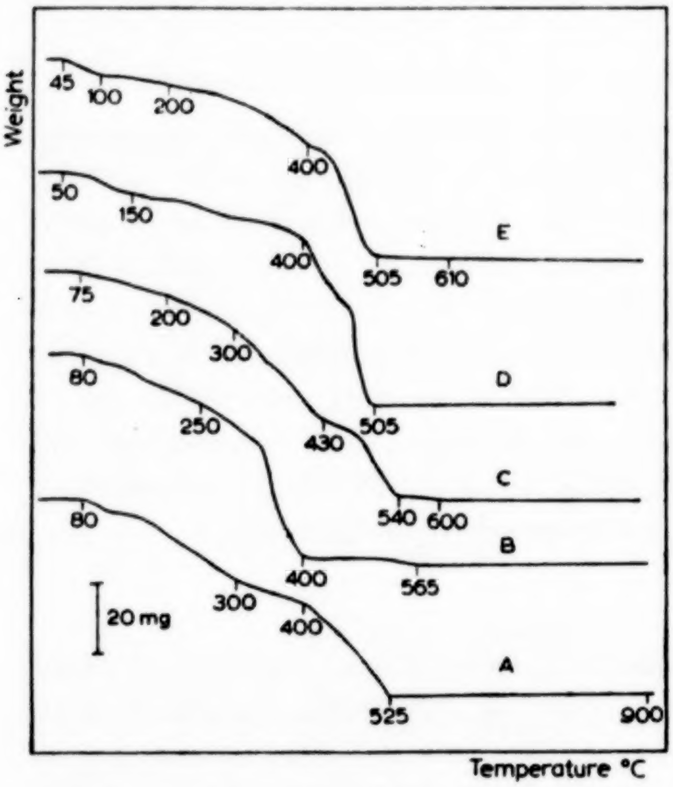

Fig. 1. Thermal decomposition of the zirconium precipitates.

A. Zirconium phthalate
B. Zirconium phenoxyacetate
C. Zirconium cinnamate
D. Zirconium diphenate
E. Zirconium 8-quinolinol chelate

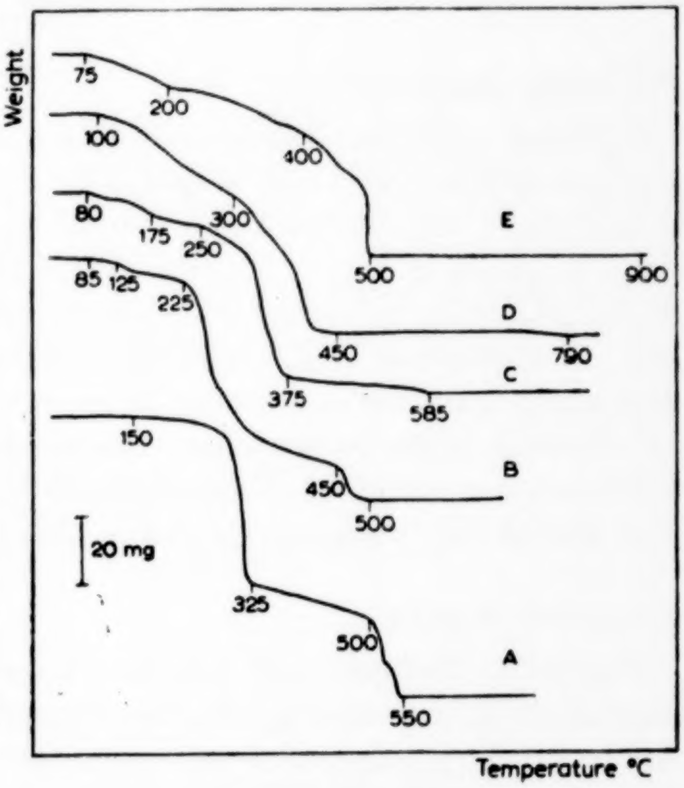

Fig. 2. Thermal decomposition of the zirconium precipitates.

A. Zirconium *p*-bromomandelate
B. Zirconium benzilate
C. Zirconium *m*-cresoxyacetate
D. Zirconium salicylate
E. Zirconium benzoate

Zirconium p-bromomandelate

DUVAL[1] claimed that the zirconium *p*-bromomandelate precipitate had a horizontal weight level from 64° to 170° but that the formula of the compound was not stoichiometric for the normal salt. He found molecular weights of 849 and 901 when the normal salt is 1015.46. It was also stated that the precipitate did not possess a definite formula and could not be made to have one. Because of this variability of composition, the precipitate was ignited to the oxide, the oxide level being obtained at 825°.

The thermal decomposition curve of zirconium *p*-bromomandelate is shown in Fig. 2. The precipitate obtained corresponded very nearly to the formula for the normal salt, $Zr(BrC_6H_4CHOHCOO)_4$, the molecular weight found was 980. The precipitate possessed the greatest thermal stability of all the zirconium salts studied.

The precipitate was stable up to 150° where it began to decompose slowly. After a period of rapid decomposition a break in the curve began at 325° and then further oxidation above 500° to give the oxide level beginning at 550°. Although DUVAL does not recommend weighing the precipitated salt directly because of variable composition, further work on the precipitation conditions should be carried out because the precipitate possesses excellent thermal stability.

Zirconium benzilate

VENKATARAMANIAH AND RAGHAVA RAO[8] used benzilic acid to separate zirconium from bivalent cations, aluminum, uranium and the cerite rare earths from solutions which were 0.2*N* or less in HCl. The composition of the precipitate was said to be $Zr(O)(OH)[(C_6H_5)_2C(OH)COO]\cdot 4\ H_2O$ after drying at 110°. KLINGENBERG, VLANNES AND MENDEL[7] could not precipitate zirconium under the conditions specified by the previous investigators. They also found that the precipitated compound was not a basic salt but had an empirical formula in the range from $ZrC_{41}H_{31}O_9$ to $ZrC_{52}H_{44}O_{12}$, the latter corresponds to the normal salt, $Zr[(C_6H_5)_2C(OH)COO]_4$. However, due to the variability of composition, the precipitate was ignited to the oxide at 1000°. The thermal decomposition curve for zirconium benzilate is shown in Fig. 2. The formula of the precipitated compound corresponded to the normal salt, $Zr[(C_6H_5)_2C(OH)COO]_4$. The precipitate was not very stable, the first weight loss occurred at 85°. Above 225° the precipitate decomposed rapidly with a break in the curve at about 450°. The remaining carbonaceous material was oxidized above 450° resulting in the oxide level beginning at 500°. It does not seem necessary to ignite the precipitate at 1000° as previously suggested to obtain the oxide.

Zirconium m-cresoxyacetate

The thermal decomposition of zirconium *m*-cresoxyacetate is shown in Fig. 2. The precipitated compound corresponded to the formula, $ZrO(CH_3C_6H_4OCH_2COO)_2$, in contrast to the formula proposed by previous investigators of $Zr(O)(OH)(CH_3C_6H_4OCH_2COO)$[15]. The precipitate was stable up to 80° where it began to decompose slowly. Beyond 250° the decomposition increased, resulting in a mixture containing carbonaceous matter at 375°. On further heating, the oxide level appeared at 585°.

Zirconium salicylate

Salicylic acid will precipitate zirconium from solutions 0.18*N* in HCl[3]. This acid has also been used in the purification of hafnium free zirconium[9]. The composition of the precipitate, as found by the latter investigators, corresponded to a ratio of 1 ZrO_2 to 1.5 salicylic acid.

The thermal decomposition of zirconium salicylate is shown in Fig. 2. The precipitated compound corresponded closely to the formula, $ZrO(HOC_6H_4COO)_2$. The precipitate was stable up to 100° where it began to decompose slowly. After various stages of decomposition the oxide level was obtained beginning at 790°.

Zirconium benzoate

The thermal decomposition curve of zirconium benzoate is shown in Fig. 2. The formula of the precipitate corresponded to the basic salt, $ZrO(C_6H_5COO)_2$. The precipitate was stable up to 75° where it began to decompose slowly. Beyond 200° the decomposition increased giving the oxide level beginning at 500°. Benzoic acid was found to precipitate zirconium quantitatively from 0.15*N* HCl solutions with effective separations from bivalent metal ions, uranium, aluminum and the rare earth elements[10].

SUMMARY

The thermal decomposition of the zirconium salts of phthalic, phenoxyacetic, cinnamic, diphenic, *p*-bromomandelic, benzilic, *m*-cresoxyacetic, salicylic and benzoic acids and 8-quinolinol were studied on the thermobalance. The precipitates exhibited varying degrees of stability with the first weight losses occurring in the temperature range of 45° to 160°. After decomposition through various intermediates, the oxide (ZrO_2) levels were obtained between 500° to 790°.

RÉSUMÉ

La décomposition thermique des sels de zirconium des acides phtalique, phénoxyacétique, cinnamique, diphénique, *p*-bromomandélique, benzilique, *m*-crésoxyacétique, salicylique et benzoïque, ainsi que de la 8-hydroxyquinoléine a été étudiée sur la thermobalance. Les précipités ont présenté des degrés de stabilité divers avec les premières pertes de poids se produisant entre les températures de 45° à 160°. Après décomposition des différents composés intermédiaires, on atteint le palier de l'oxyde (ZrO_2) entre 500° et 790°.

ZUSAMMENFASSUNG

Die thermische Zersetzung der Zirkoniumsalze von Phtalsäure, Phenoxyessigsäure, Zimtsäure, Diphensäure, *p*-Bromomandelsäure, Benzilsäure, *m*-Cresoxyessigsäure, Salizylsäure und Benzoësäure sowie von 8-Hydroxychinolin wurde auf der Thermowaage untersucht. Die Niederschläge zeigen verscheidene Beständigkeit; die ersten Gewichtsverluste treten zwischen 45 und 160° auf. Nach Zersetzung verschiedener Zwischenprodukte wird das Oxyd (ZrO_2)-Niveau zwischen 500 und 790° erreicht.

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THE ANALYSIS OF HALOGENATED HYDROCARBONS BY VAPOUR PHASE CHROMATOGRAPHY

by

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Previous work on the separation and analysis of certain halogenated hydrocarbons by adsorption chromatography has been reported by JANÁK[1], CLAESSON[2], CREMER[3], and JAMES AND PHILLIPS[4]. On gas-liquid partition columns, PURNELL AND SPENCER[5a] used solubilising agents for the improvement of the separation of chloro-methanes, and more recently[5b] discussed the temperature dependence of this group when liquid paraffin was used as the stationary phase on kieselguhr. Factors affecting the elution order and retention volumes of a series of chloro- and fluoro-chloro-methanes on columns with stationary phases of dibutyl phthalate, dinonyl phthalate, glycerol, and silicone fluids respectively have been described by us in a previous paper[6].

The purpose of this communication is to describe the separation of a wide range of halogenated hydrocarbons by partition chromatography with stationary phases of different types and over a range of column temperatures. The data from these experiments can be used for the identification of halogenated hydrocarbons using a method originally described by LITTLEWOOD *et al.*[7] for other compounds. Since this work was completed, retention volumes for a number of halogenated hydrocarbons have also been recorded on gas-liquid partition columns by HARRISON[8], of fluoro-chloro-methanes by GREEN[9], and of highly fluorinated hydrocarbons by EVANS AND TATLOW[10]. In an appendix, heats of solution are calculated and compared with the latent heat of vaporisation for several halogenated hydrocarbons.

More stringent operating conditions are required for quantitative analysis than for a qualitative separation. In the second part of this paper, operating conditions are investigated as well as factors affecting the accuracy of quantitative analysis using an internal standard.

PART I. QUALITATIVE SEPARATIONS

The apparatus and experimental procedure have been described in a previous paper.

To avoid asymmetrical peaks due to overloading of columns, quantities of 0.5-1 μl of liquids were injected from a micrometer syringe, or 0.1-0.3 ml N.T.P. of gases were admitted to the top of the column from a gas burette. The retention time to the maximum point of the peak was determined for each substance injected separately, and the corrected retention vol./g stationary phase (V_g) was calculated.

Results

Table I summarizes the results of preliminary work on the separations of a variety of mixtures, some of which were synthesized from pure materials, while others were commercially available.

TABLE I

TYPICAL SEPARATIONS

	Conditions			*Mixture separated in order of elution*				
Stationary Phase	*Wt. of liquid g*	*Temp. °C*	*Flow rate ml N_2 min*	*Compound and retention time in minutes*				
Dibutyl phthalate	4.0	21	25	CF_3Cl 1.9	CF_2Cl_2 3·75	$CFCl_3$ 20.6		
	1·5	21	56	CF_2Cl_2 1.6	$CFCl_3$ 4·7	CH_2Cl_2 15.8	CCl_4 30.6	$CHCl_3$ 47·5
	1·5	19	32	$CClF_2{\cdot}CClF_2$ 3·75	$CClF_2{\cdot}CCl_2F$ 21.1			
	1·5	56	32	$CClF_2{\cdot}CClF_2$ 1.6	$CClF_2{\cdot}CCl_2F$ 4·2	Unknown 10.8	$CCl_2F.CCl_2F$ 21.1	
Dinonyl phthalate	2.0	24	13·5	CF_3Cl 2.8	CF_2Cl_2 4.0	$CFCl_2H$ 5·4	$CFCl_3$ 16.9	$CFCl_2H$ 23·4
	2.0	77	60	*trans*-dichloro-ethylene 2.8	*cis*-dichloro-ethylene 4.6	trichloro-ethylene 7·5	tetrachloro-ethylene 15.0	
Silicone 702	2.14	77	30	CH_3Br 1·5	CH_2ClBr 4·5	CH_2Br_2 8.6	$CHBr_3$ 38·5	
	2.14	77	18	*trans*-dichloro-ethylene 20.1	*cis*-dichloro-ethylene 29·5			

A specimen of $CFCl_2{\cdot}CFCl_2$ contained three more volatile substances, two of which wee identified as $CFCl_2{\cdot}CF_2Cl$, and $CF_2Cl{\cdot}CF_2Cl$, and the analysis of fractionally distilled $CFCl_2{\cdot}CF_2Cl$ showed the presence of two more volatile impurities, one of which was $CF_2Cl{\cdot}CF_2Cl$.

The separation of *cis*- and *trans*-dichloroethylene has been reported[7]. Our work shows that the *trans*-isomer (b.p. 48.3°C) is eluted before the *cis*-isomer (b.p. 58.8°C) on silicone 702, which is in the reverse order to that quoted above[7].

Studies of mixtures of CH_2Br_2 and CH_2ClBr have established that less than 0.1% of each substance in the other can be determined.

Column temperature variation

Figs. 1-3 present the corrected retention volume/g for a number of halogenated hydrocarbons on columns with different stationary phases over a range of temperature (20°-100°C).

The identification of an unknown volatile compound

The V_g values presented above can be used for the identification of unknown substances without reference to other physical constants, such as m.p. or b.p. It is

References p. 143

essential, however, that the conditions for operating the chromatographic elution should be standardized. The reproducibility of V_g values on different columns of the same static liquid phase has been determined[7]. V_g values on silicone fluid 702 were reproducible to ± 4% for variation in packing density and for different batches of silicone fluid. This corresponds to 0.02 log units and gives sufficient accuracy for most purposes, though with an internal standard they claim a reproducibility of ± 1%. While results on different columns only agree to ± 4%, V_g values on one column are more reproducible, especially if column temperature, flowrate, and injection procedure are carefully controlled. Variations due to these factors may also be reduced by using an internal standard. However, for chloromethanes with acetone as the internal standard, the ratio of the retention volume of a chloromethane to that of acetone varies with the temperature of injection of the sample[6,8]. It is therefore necessary to inject samples at a constant temperature to obtain good reproducibility.

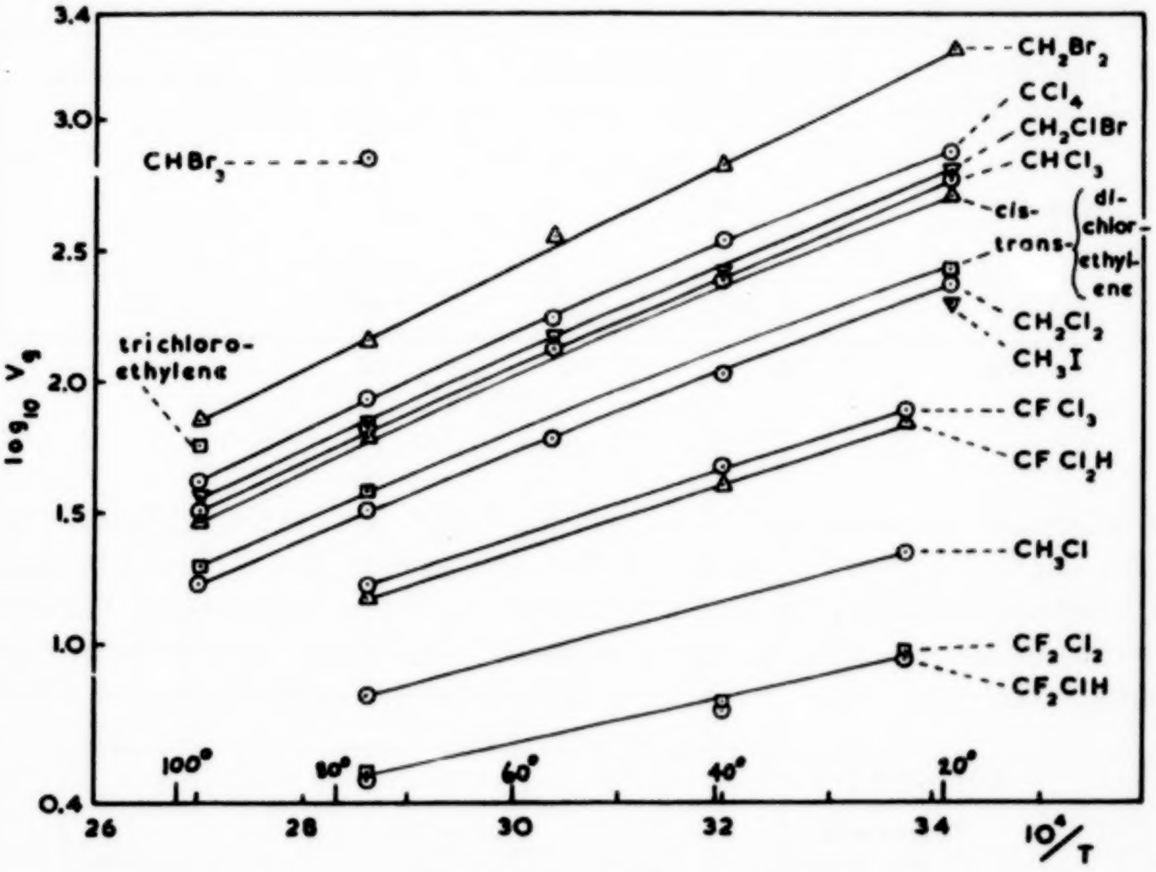

Fig. 1. Silicone fluid 702.

The correction for asymmetry of peaks by an empirical procedure[7] has not been found to hold for chloromethane peaks, which are asymmetrical in the opposite direction to alcohol peaks. For any slight asymmetry, the correction was less than 1% for the above chloromethanes provided that a sample of less than 1 μl of each component was injected under our operating conditions.

From work previously reported by us[6], it was established that V_g values may sometimes be dependent upon the amount of liquid phase on the column. For example, with chloromethanes on water partition columns, V_g values depended upon the amount of water, but this was not so for the same substances on dinonylphthalate columns. The data recorded in Figs. 1 and 2 were obtained on a number of columns with different amounts of liquid phase, and V_g values were independent of the amount of stationary phase. The results in Fig. 3 have only been obtained on one column containing 2.3 g of glycerol.

With a series of plots such as Figs. 1-3, the identification of any individual member of this group can be achieved. The V_g value can be determined on one column at one temperature and the point located on the $\log_{10} V_g$-$1/T$ plot for that column. The identification can be checked by examining the same sample at a different temperature, or on a different column. For such a scheme to be widely applicable, a knowledge of V_g values for all possible vapours is desirable, and owing to the many variables operating, these have to be determined experimentally under controlled conditions.

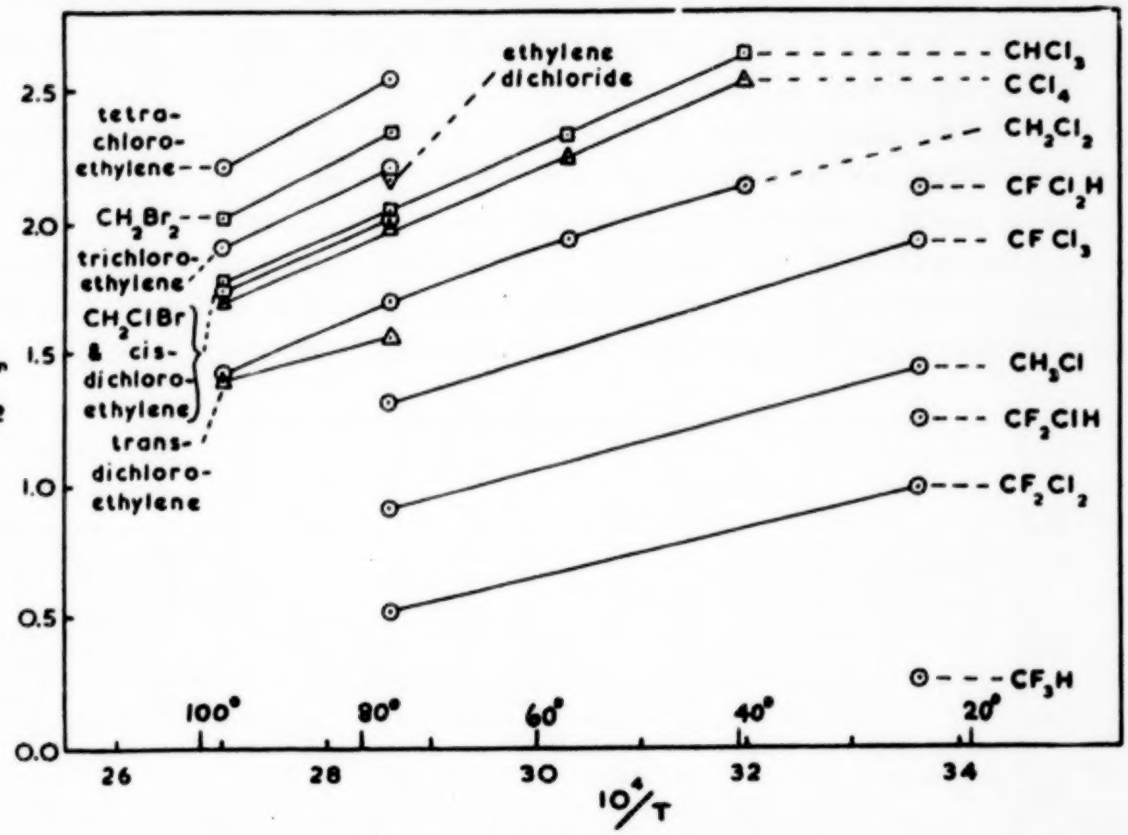

Fig. 2. Dinonyl phthalate.

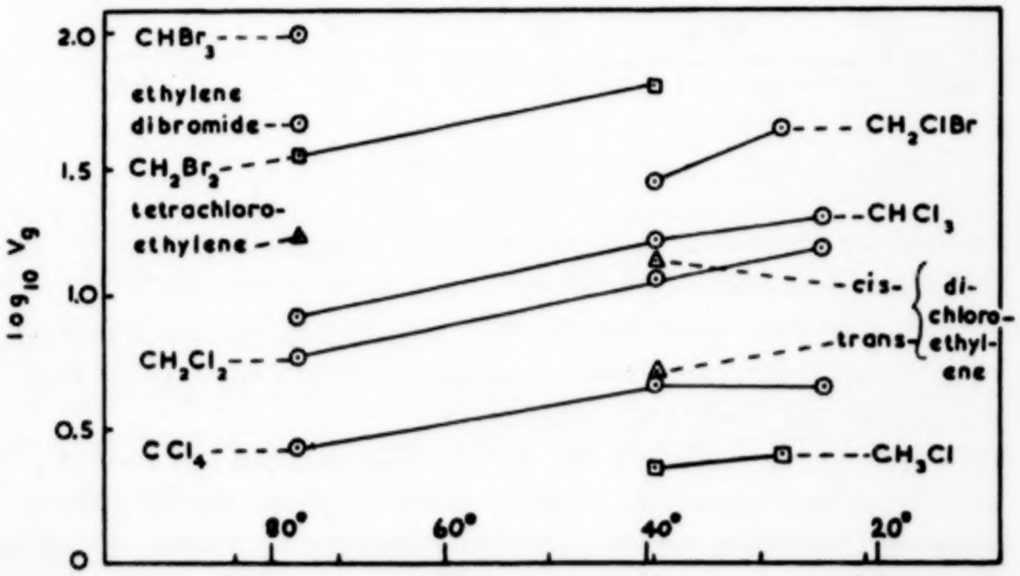

Fig. 3. Glycerol.

It has been shown[7] that a very good estimate for V_g values can be obtained by an extrapolation of a plot of $\log_{10} V_g$ against the number of carbon atoms for a homologous series, such as *n*-alcohols. JAMES[12] and MARTIN[13] have described other methods which are applicable to hydrocarbons, halides, amines, ketones, alcohols, ethers, esters, and nitro compounds.

PART II. QUANTITATIVE ANALYSIS

An internal standard in quantitative analysis was first used by RAY[14] and later by BRADFORD *et al.*[15], CROPPER AND HEYWOOD[16], and more recently by DIMBAT *et al.*[17]. In this section we have applied the internal standard method to mixtures of halogenated hydrocarbons taking a mixture of chloromethanes as a typical example.

Acetone was found to be a suitable internal standard for this mixture, since it has the same order of boiling point as the components of the mixture, and it can be completely separated from them without overlap on a dinonyl phthalate partition column (see Fig. 4). Ideally the internal standard should have a similar chemical structure to that of the type of compounds with which it is used, but this is not essential.

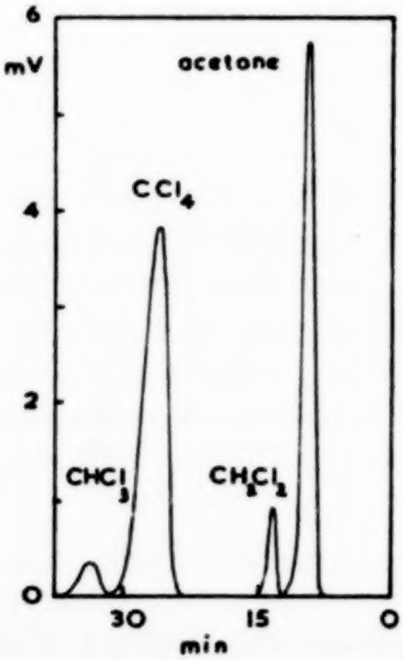

Fig. 4. Calibration chromatogram. 10% CH_2Cl_2, 10% $CHCl_3$, 80% CCl_4.

From a trial elution on a column of 2 g dinonyl phthalate on celite 545, the following conditions were selected as the best: flowrate, 30 ml N_2 per minute; column at 40°C; catharometer at 36°C with 70 mA total bridge current; recorder speed was set at its maximum of 16″ per hour. The temperature of the injection port was maintained at 50°C, since this had previously been shown to affect peak height and efficiency[11]. These conditions gave a complete separation of the three chloromethanes and the standard, and maximum recorder deflection was given for 5 µl of dichloromethylene.

To establish how accurately conditions must be controlled, a series of experiments was carried out with a mixture of equal parts by volume of dichloromethylene and acetone. The recorder response was assumed to be constant, and the bridge current of the catharometer could be set daily to better than 1% by using a 0-12 mV meter with a 6″ scale across a 0.1 Ω resistor in the bridge circuit. Since the temperature variation of the vapour-jacketed column and catharometer was very small, effects due to this will not be considered here.

The following factors were varied:

(a) Flowrate. The increase in the ratio of the height of the elution peaks to the height of the standard peak was approximately 1.5% per 1% increase in flowrate over the range 27-33 ml N_2 per minute. However, the ratio of areas showed a random variation of ± 2% over the same range with a maximum variation of 4% from the mean.

(b) Volume of sample. When the volume of sample injected was varied in the range 7 µl to 11 µl, the ratio of areas varied randomly by ± 4%, while the ratio of heights varied only ± 0.6% with a maximum deviation of 2%.

(c) Injection temperature. Variation from 40°-65°C gave a random variation of ± 1.2% for the ratio of peak heights, and ± 3% for the ratio of areas.

For the determination of the calibration curves and the analysis of synthetic mixtures, the operating conditions were maintained within the following limits: flowrate ± 1%; volume injected, ± 5%; temperature of injection, ± 2°C; column temperature, ± 0.2°C.

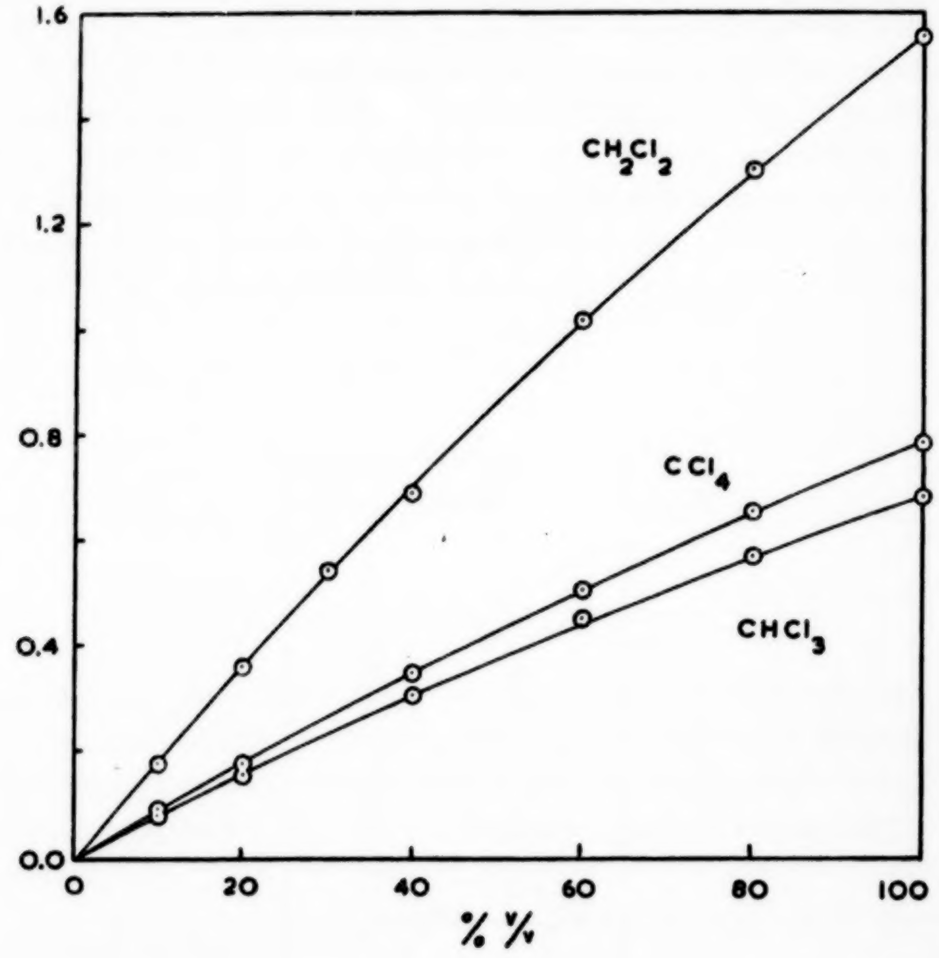

Fig. 5. Calibration curves for ratio of heights method.

Mixtures of the three chloromethanes were made up in various simple proportions, and an equal volume of acetone was added to each mixture. For each analysis, a volume of 10 µl was injected into the column using an Agla micrometer syringe fitted with an 18 gauge steel needle.

The height of each elution peak was measured with an accurate scale (1″ = 1 mV), while the area was found by (a) a precision disc planimeter (Stanley and Co., London) and (b) multiplying the height by the width at half the maximum height (*cf.* CREMER *et al.*[3]).

The ratios of peak heights and peak areas were calculated for each chloromethane with respect to the internal standard, *i.e.* acetone. The data were plotted against the percentage composition to give a calibration curve for each chloromethane. Fig. 5 shows the calibration curves for height ratios, since this method was found to be quicker and to give more consistent results than the methods based upon area measurements. Of the two methods used for area determinations, the planimetric method is very tedious, and the results do not justify its use in place of the width × height method. DIJKSTRA *et al.*[18] claim that measurement of areas by a weighing method has advantages also over the planimeter in both speed of determination and accuracy. LICHTENFELS *et al.*[19] measured areas with a planimeter and quoted average deviations of 0.4 to 0.6 mole % for blends of C_5 and C_6 hydrocarbons. These figures refer to absolute mole %, since certain peaks gave differences between the blended and observed values of up to 16% of the blended value.

References p. 143

The results of the analyses of synthetic mixtures are given in Table II. With the ratio of heights method, the deviation of the amount of the component found from the amount present was usually under 2%, although with the lowest amounts of each component (8.3% v/v), the deviation was 4%. The standard deviations for three determinations was 0.5-3% with an average value of 1.4%. The results for area method were less consistent, and for some the standard deviation for three determinations was of the order of 5%, with an average of 3.6%.

TABLE II

		Width × height method			*Planimeter area method*			*Ratio of heights method*		
Components	*% v/v taken*	*% v/v found*	*Deviation % found % taken (%)*	*Standard deviation 3 detmns. (%)*	*% v/v found*	*Deviation % found % taken (%)*	*Standard deviation 3 detmns. (%)*	*% v/v found*	*Deviation % found % taken (%)*	*Standard deviation 3 detmns. (%)*
CH_2Cl_2	25.0	24.7	—1.2	4.8	24.8	—0.8	4.7	25.0	0.0	0.7
CCl_4	25.0	24.3	—2.8	4.7	24.3	—2.8	3.5	24.9	—0.4	1.8
$CHCl_3$	50.0	47.4	—5.2	3.4	49.9	—0.2	1.6	48.9	—2.2	1.3
CH_2Cl_2	83.33	85.0	+2.0	1.9	85.5	+2.9	3.3	84.3	+1.2	0.5
CCl_4	8.33	8.0	—4.1	3.0	8.5	+2.0	4.5	8.0	—4.1	0.5
$CHCl_3$	8.33	7.3	—13	0.9	7.6	—8.8	9.6	8.0	—4.1	1.5
CH_2Cl_2	12.5	12.1	—3.2	1.0	12.4	—0.8	2.1	12.3	—1.6	3.1
CCl_4	75.0	73.6	—1.9	3.4	72.5	—3.3	2.5	73.7	—1.8	2.2
$CHCl_3$	12.5	12.4	—0.8	5.3	13.0	+4.0	5.5	12.7	+1.6	1.0

Since this work was completed, DIMBAT *et al.*[17] have pointed out the advantages of using helium as the carrier gas instead of nitrogen. The greater difference between the thermal conductivity of helium and organic molecules enables the catharometer to function with almost equal sensitivity for each species. The areas under the peaks were related to the sample composition without prior calibration, and gave standard deviations of 6.8-9.8%, depending upon the method of area measurement. Improved accuracy was achieved by calibration and gave a standard deviation of 0.76%.

APPENDIX

Heats of solution in the liquid phase

The following formula[7] has been used for these calculations:

$$\triangle H = -2.3R \text{ (gradient)} + RT^2 \ln \varrho / \mathrm{d}T$$

where $\triangle H$ is the heat of solution of a vapour in the static liquid phase, ϱ is the density of the liquid phase, T is the temperature, R the gas constant, and (gradient) is the gradient of the plot of $\log_{10} V_g$ against $1/T$. The last term can be calculated from the cubical expansion coefficient of the column liquid and the value for this term is —0.16 kcal (the negative sign indicating a numerical increase in the value of the heat of solution). Table III gives a number of heats of solution in silicone 702. Wherever the plots are slightly curved, the value of the gradient is taken at the b.p. of the vapour in question. Table III also gives the values for the latent heat of vaporisation (L) at the b.p., and the ratio of $\triangle H/L$.

TABLE III

Vapour	*Heat of solution in silicone 702 kcal/mole*	*Latent heat of vaporisation at b.p. kcal/mole*	*ΔH/L*
CH_2Cl_2	7.3 ± 0.3	6.68	1.09
$CHCl_3$	8.2 ± 0.3	7.05	1.16
CCl_4	8.8 ± 0.3	7.13	1.24
trans-dichloroethylene	7.4 ± 0.6	7.23	1.02
cis-dichloroethylene	8.3 ± 0.6	7.15	1.16

The heat of solution for *trans*-dichloroethylene is in good agreement with the latent heat at the boiling point, but the values for *cis*-dichloroethylene and the chloromethanes are significantly higher than the latent heat. Heats of solution in silicone 702 have been compared[7] with latent heats for alcohols, acetates, benzene, and toluene. Ethanol and propanol had heats of solution significantly lower than the latent heats, while the other compounds had values in good agreement. However, on a tri-tolyl phosphate liquid phase, heats of solution were higher than latent heats for acetates, benzene, and toluene, but lower for ethanol and propanol. Recently HOARE AND PURNELL[5b] have obtained heats of solution for several chloro-hydrocarbons on a liquid paraffin column. They found that CH_2Cl_2, $CHCl_3$, and CCl_4 have heats of solution slightly lower than the latent heats, while *cis*- and *trans*-dichloroethylene have considerably lower heats of solution than latent heats. They attribute this to positive deviation from Raoult's law.

All these compounds on a silicone 702 column give a ratio of $\triangle H/L$ greater than 1 (Table III) and can be considered to show negative deviation from Raoult's law. On a dinonyl phthalate column, CH_2Cl_2 has a heat of solution of approximately 5.4 kcal/mole ($\triangle H/L = 0.81$) and shows significant positive deviation. $CHCl_3$ gave $\sim$ 8.0 kcal/mole ($\triangle H/L = 1.13$), and $CCl_4 \sim 7.8$ kcal/mole ($\triangle H/L = 1.09$) and both show negative deviation. On a glycerol column, the limited number of results available show that low heats of solution are given by all the halogenated compounds studied, *e.g.* $CH_2Cl_2 \sim 2.6$ kcal/mole.

ACKNOWLEDGEMENTS

The authors wish to thank the National Smelting Co., Avonmouth, England, and the Imperial Chemical Industries, Ltd., for gifts of halogenated hydrocarbons, and one of them (C.J.H.) thanks Messrs. British Celanese, Ltd., for a Senior Research Studentship, during the tenure of which the above work was carried out.

SUMMARY

The separation of a range of halogenated hydrocarbons by gas-liquid partition chromatography with various stationary phases is described. The data are presented as plots of the logarithm of the corrected retention volume per gram of stationary phase against the inverse of the column temperature, and can be used for the identification of these substances. Heats of solution in the liquid phase are calculated and compared with the latent heats of vaporization.

The selection of operating conditions to separate and quantitatively analyse mixtures of liquid halogenated hydrocarbons is described. Factors affecting the accuracy of analysis using an internal standard are discussed. A comparison is made of the accuracy and reproducibility of the results obtained by three methods of calibration.

RÉSUMÉ

Les auteurs décrivent la séparation d'une série d'hydrocarbures halogénés par chromatographie de partage gaz-liquide, en utilisant différentes phases stationnaires. Les graphiques obtenus (logarithme du volume de rétention corrigé par gramme de phase stationnaire, en fonction de l'inverse de la température de la colonne) peuvent être utilisés pour l'identification de ces substances. Les chaleurs de dissolution dans la phase liquide sont calculées et comparées avec les chaleurs latentes de vaporisation.

On décrit également le choix des conditions opératoires pour séparer et analyser quantitativement des mélanges d'hydrocarbures halogénés liquides. Les facteurs influençant la précision des analyses lors de l'emploi d'un étalon interne sont discutés. Une comparaison est faite sur la précision et la reproductibilité des résultats obtenus par trois méthodes d'étalonnage.

ZUSAMMENFASSUNG

Eine Methode zur Trennung einer Reihe von halogenierten Kohlenwasserstoffen durch Gas-Flüssigkeit-Verteilungschromatographie mit verschiedenen stationären Phasen wird beschrieben. Die erhaltenen Diagramme (Logarithmus des korrigierten zurückgehaltenen Volumens pro Gramm stationäre Phase in Funktion des umgekehrten Wertes der Säulentemperatur) können zur Identifizierung dieser Substanzen dienen. Die Lösungswärmen in der flüssigen Phase wurden berechnet und mit den latenten Verdampfungswärmen verglichen.

Die Wahl der Arbeitsbedingungen zur Trennung und quantitativen Analyse von Gemischen flüssiger halogenierter Kohlenwasserstoffe wird ebenfalls beschrieben. Die Faktoren, welche die Genauigkeit der Analyse bei Verwendung einer inneren Vergleichssubstanz beeinflussen, werden erörtert. Die Genauigkeit und Reproduzierbarkeit der mit drei Eichmethoden erhaltenen Resultate wird verglichen.

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ANALYSIS OF MIXTURES OF GLYCOLS BY ION-EXCHANGE CHROMATOGRAPHY

by

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In previous reports, the authors have developed a procedure for the determination of polyols by dichromate oxidation[1], and investigated the elution behavior of the glycols with the application of the plate theory of ion-exchange chromatography[2,3]. An equation describing the elution behavior of the glycols was derived[2]

$$\frac{WQ[\mathrm{RBO_2}]}{CV} = \frac{K_1[\mathrm{BO_2^-}]}{K_2} + \frac{1}{K_2}$$

where W is the weight of the resin in grams, Q is the exchange capacity per gram of resin, $[\mathrm{RBO_2}]$ is the mole fraction of the resin in the borate form, C is the distribution ratio of the glycol[2], and V is the interstitial volume of the column of resin. The equation was used to evaluate the complexing constants K_1 and K_2 for the reactions between the glycol and the borate ion in solution and on the resin respectively. Then the elution equation and the complexing constants were used to calculate the conditions necessary for the separation of diethylene glycol, ethylene glycol, 1,2-propylene glycol, the *meso* and the dl isomers of 2,3-butylene glycol, and glycerol[3]. In this paper, experimental procedures and analytical results of the method chosen for the analysis of a glycol mixture are reported.

APPARATUS AND REAGENTS

Apparatus for the collection of small fractions of column effluent has been described[4].

Absorbance measurements were made with a Beckman quartz spectrophotometer, Model DU, equipped to receive 10-cm silica cells.

Two columns with an internal cross-sectional area of 2.28 sq. cm were used. The first was filled with 76.5 cm of Dowex 1-X8, 200-300 mesh, which had previously been converted to the borate form. The second was similarly packed with 20 cm of Dowex 1-X8 that had been equilibrated with $0.020M$ solution of borax (sodium tetraborate decahydrate).

Two eluants were required for analysis. The first $0.925M$ with $\mathrm{NaBO_2}$ and $0.0004 \pm 0.0002M$ with sodium hydroxide. (The quantity of sodium hydroxide was determined by the saturation of a portion of eluant with mannitol and the potentiometric titration with hydrochloric acid to a pH of 9.2.) The second eluant was a $0.020M$ solution of borax.

The resin, Dowex 1-X8, 200-400 mesh (dry-screened) was wet-screened through 200 mesh to remove the fine particles which cause a large pressure drop. The resultant resin, approximately 200-300 mesh (when dry) was converted to the desired form before use. In order to avoid the use of large quantities of the eluants, all of the resin was converted from the chloride to the hydroxide form by the passage of 20 ml of $5M$ carbonate-free sodium hydroxide per meq of resin. Portions of the resin were then easily converted to the borate and borax forms by the passage of either $0.925 M$ sodium borate or $0.020 M$ borax in an amount which contained three times the number of milliequivalents of resin.

A column of 80 cm × 2.28 sq. cm was packed with 76.5 cm of the converted resin by pouring the resin, slurried with the $0.925 M$ sodium borate eluant into the column and draining off the excess solution. One liter of the eluant was passed through the column at the maximum flow rate to insure complete packing of the resin. Another column of 25 cm × 2.28 sq. cm was similarly packed with 20.0 cm of resin which had been previously equilibrated with $0.020 M$ borax.

Stock solutions of the glycols, approximately $2N$ as reducing agents, were prepared and standardized by the recommended procedure. Diethylene glycol (DEG), ethylene glycol (EG), and 1,2-propylene glycol (PG) were obtained from Eastman and used without further purification. Glycerol (GL) from J. T. Baker Chemical Company was also used without further purification. Three samples of 2,3-butylene glycol (BG) were used. The first from E. I. du Pont de Nemours was a mixture of *meso* (*m*) and dl isomers. The second from the National Research Council of Canada was found to be a mixture of *meso* and *l* isomers. The third sample, technical 2,3-butylene glycol from the Celanese Corporation of America, was chromatographed and found to be a mixture of 95.0% *meso* and 3.2% dl isomers with 1.8% (based on the reducing capacity) of an oxidizable impurity of undetermined nature.

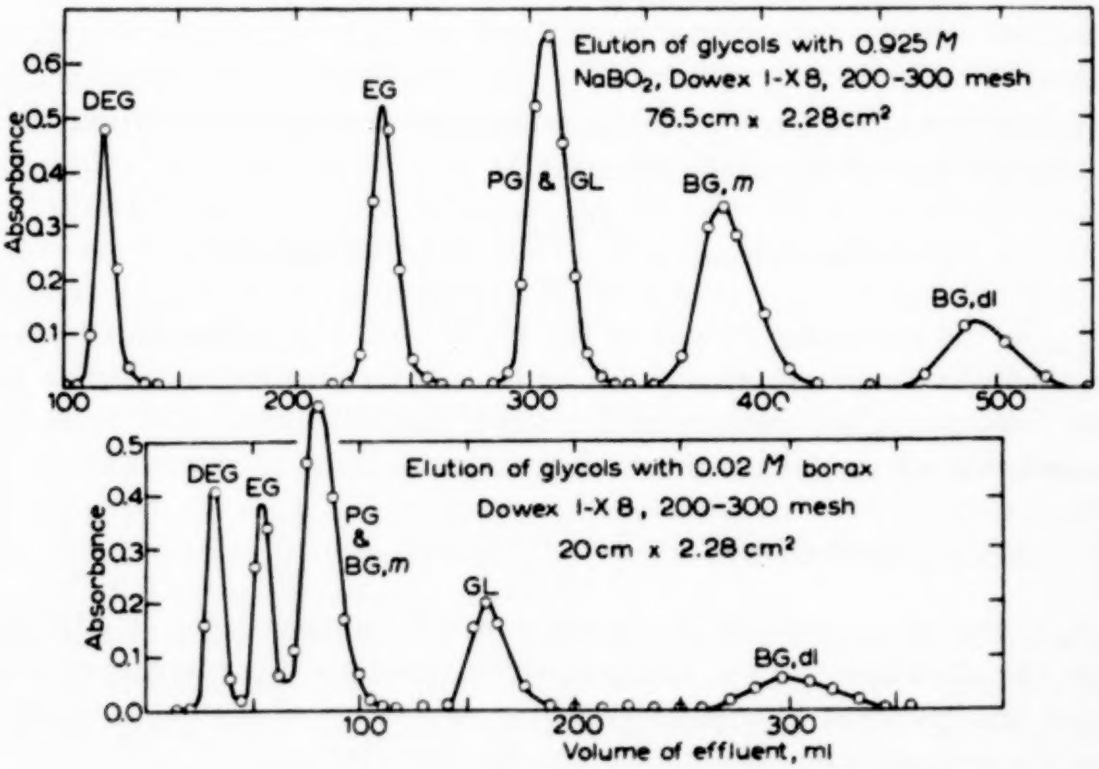

Fig. 1.

ELUTION GRAPHS

Figure 1 represents the quantitative separation of diethylene glycol, ethylene glycol, 1,2-propylene glycol, the *meso* and the dl isomers of 2,3-butylene glycol, and glycerol. Under these conditions, two elutions furnish all the data that are needed for the complete analysis of a mixture which contains the six glycols mentioned above. The elution graphs were obtained by the collection of small fractions with a fraction collector, The fractions (usually 6 ml) were mixed with a constant volume (usually 5 ml) of oxidizing reagent[1], cooled, and diluted with 25.00 ml of water before measurement of the absorbance at 610 mμ against a blank (a fraction, which is known not to contain a glycol, mixed with the oxidizing reagent and diluted).

METHOD OF ANALYSIS

The sample was dissolved in water. An aliquot of 2 ml containing in general, not more than 10 mg of any one glycol was carefully transferred to the top of the resin bed. The sample was drained at a flow rate of 0.5 cm per minute into a 100-ml graduated cylinder. Two 2-ml portions of the eluant were used to wash down the inside of the column. The sample was then eluted at a flow rate of 0.5 cm per minute. The effluent from the elution with 0.925M sodium borate was collected in successive fractions of 100, 60, 60, 60, 70, 95, and 95 ml. These contain, respectively, blank, diethylene glycol, blank, ethylene glycol, a mixture of 1,2-propylene glycol and glycerol, the *meso* isomer of 2,3-butylene glycol, and the dl isomers of 2,3-butylene glycol. The effluent from the elution with 0.020M borax was similarly collected in successive fractions of 125, 75, 55, 95, and 35 ml. The first fraction which contained diethylene glycol, ethylene glycol, 1,2-propylene glycol, and the *meso* isomer of 2,3-butylene glycol was discarded. The second, third, fourth, and fifth fractions contained, respectively, glycerol, blank, the dl isomers of 2,3-butylene glycol, and blank.

The isolated glycols were transferred quantitatively to 100-ml volumetric flasks and diluted to the mark with water. The quantity of glycol present was determined by oxidizing two 25.00-ml aliquots by the recommended procedure[1]. It was found necessary, however, to dilute the samples obtained from the elution with 0.925M sodium borate with 25.00 ml of 50% sulfuric acid to prevent the precipitation of boric acid.

Calculations

The quantity of an isolated glycol in milligrams was calculated from the absorbance A, at 610 mμ, by use of the equation

$$\text{mg glycol} = \frac{AW_m}{10\ an} \times \text{dilution factor}$$

where W_m is the molecular weight of the glycol, n is the reduction capacity[1], and a is the absorptivity previously found[1] to be 0.1487. The dilution factor was 6.12 and 4.00, respectively for elutions with 0.925M sodium borate and 0.020M borax. The quantity of 1,2-propylene glycol was obtained from the equation

$$\text{mg 1,2-propylene glycol} = \left(\frac{A_1}{1.487} \times 6.12 - \frac{A_2}{1.487} \times 4.00\right)\frac{W_m}{n}$$

where A_2 is the absorbance of the fraction which contained the isolated glycerol, and A_1 is the absorbance of the fraction which contained the mixture of 1,2-propylene glycol and glycerol. The quantity of the dl isomers of 2,3-butylene glycol was taken as the average value obtained from the two elutions.

RESULTS

The results shown in Table I were obtained by subjecting three known mixtures to analysis. Mixture 1 was analysed four times and the results were used to find the standard deviation, σ, for the determination of each glycol. Duplicate analyses were run on mixtures 2 and 3. Mean values for all mixtures were reported.

TABLE I

	Mixture 1 (55.90 mg)			*Mixt. 2 (25.27 mg)*		*Mixt. 3 (26.12 mg)*	
Glycol	*Taken mg*	*Found mg*	σ	*Taken mg*	*Found mg*	*Taken mg*	*Found mg*
DEG	5.99	5.98	0.03	4.38	4.39	1.00	0.99
EG	8.33	8.60	0.24	0.61	0.59	13.88	13.86
PG	9.13	9.13	0.20	6.68	6.65	1.52	1.48
GL	8.95	8.71	0.07	6.65	6.38	1.49	1.50
BG, *m*	23.50	16.73	0.07	7.05	0.17	7.81	7.51
BG, dl		6.70	0.25		6.77	0.26	0.12

A different source of 2,3-butylene glycol was used in each of the three analyses. Mixture 1 contained 2,3-butylene glycol from Du Pont and was found (Table I) to consist of 70.2% *meso* and 29.8% dl. The 2,3-butylene glycol in mixture 2, obtained from the National Research Council of Canada was found to be a mixture of 1.4% *meso* and 98.6% of the l isomer. The 2,3-butylene glycol from Celanese was previously chromatographed because of an oxidizable impurity which is eluted with glycerol with a 0.020*M* borax eluant and with the dl isomers of 2,3-butylene glycol in the elution with 0.925*M* sodium borate. Corrections for this impurity have been applied to the quantity found for glycerol and the dl isomers of 2,3-butylene glycol in mixture 3 of Table I.

DISCUSSION

With the exception of distillation, chromatographic procedures are the only known methods for the separation of glycol mixtures prior to analysis. The authors have reported the separation of diethylene glycol from dipropylene glycol[5] by a technique designated as salting-out chromatography. DAL NOGARE[6] employed partition chromatography for the separation of 1,2-propylene glycol, 2,3-butylene glycol, and 1,2-butylene glycol from ethylene glycol on silicic acid-celite columns. Fractions which contained the first three glycols were analysed by oxidation with periodate. In general, recoveries of 90 to 110% were found for 4 to 20 mg of each glycol determined.

In the method of analysis discussed in this paper, the time required for the elutions, when run simultaneously, was 10 hours. An analyst might prefer to decrease the flow rate of the longer elution (with 0.925*M* sodium borate eluant) from 0.5 to 0.3 cm per minute so that an overnight elution, which requires no attention, may be run. The fractions of effluent, collected with the aid of a fraction collector, could then be mixed and analysed.

It is not unusual for two batches of the same commercial resin to vary in both capacity and crosslinking. The batch of Dowex 1-X8 (lot No. 3902-30) used to obtain the foregoing data was found to differ appreciably from the resin that was used for the theoretical study of the elution behavior of the glycols[2] (lot No. 1196-24). For example, the concentration of sodium borate which was predicted to produce the separation described above was 0.75*M*. This was confirmed[3] by quantitative separations obtained with Dowex 1-X8, lot No. 3589-27, on a 50 cm × 2.28 sq. cm column. With this resin, the separation of the glycols was accomplished in 6 hours with a column height of 50 cm. Therefore, it is necessary that the elution characteristics of a given batch of resin be investigated in order that quantitative separations may be obtained.

Dowex 1 resins are subject to a slow decomposition in solutions of high pH. The exchange capacity is lowered by the formation of free amine from the quaternary-ammonium groups which serve as the exchange sites on the resin matrix. Over a period of one month, twenty elutions were run which required the passage of approximately 15 liters of 0.925*M* sodium borate. After this period, a redetermination of the elution graph of the mixture showed that the peaks were shifted toward the left. The differences between the peaks before and after this one-month period were found to be 3, 9, 13, 24, and 31 ml of effluent for DEG, EG, PG and GL, BG *m*, and

References p. 148

BG dl, respectively. The useful life of the resin may be extended by an increase in column height with periodic changes in the cut points. No decomposition was discernible for resin equilibrated with 0.020 M borax over a period of 6 months.

SUMMARY

Procedures and results of the anion-exchange separation of diethylene glycol, ethylene glycol, 1,2-propylene glycol, the *meso* and the dl isomers of 2,3-butylene glycol, and glycerol are reported. This separation allows the determination of each of the six compounds present in the mixture by oxidation with dichromate.

RÉSUMÉ

Une méthode est décrite pour la séparation à l'aide d'une résine échangeuse d'anions de chaque constituant d'un mélange de diéthylèneglycol, éthylèneglycol, 1,2-propylèneglycol, *meso*-2,3-butylèneglycol, dl-2,3-butylèneglycol et glycérine. Le dosage de chaque glycol s'effectue après séparation par oxydation au moyen de dichromate.

ZUSAMMENFASSUNG

Nach der Trennung durch Anionenaustauschchromatographie eines Gemisches von Diäthylenglykol, Äthylenglykol, 1,2-Propylenglykol *meso*-2,3-Butandiol, dl-2,3-Butandiol und Glycerin, wird jedes Glykol durch Oxydation mit Dichromat bestimmt.

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A RAPID COLORIMETRIC METHOD FOR THE DETERMINATION OF ALUMINIUM IN Cu-Al ALLOYS

by

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This method was developed for the analysis of aluminium brasses and bronzes. It was designed as a rapid routine method. The procedure described is for the 2% aluminium brasses, but slight modifications such as the aliquot taken for development of colour makes it applicable to the aluminium bronzes.

Procedure

Dissolve 1 g alloy in 10 ml nitric acid and dilute to 100 ml in a graduated flask. Pipette a 10 ml aliquot into a 100 ml beaker and add 5 ml sodium hydroxide solution. Boil 1 to 2 minutes, cool and dilute to 100 ml in a graduated flask. Allow the precipitate to settle (filter some of it if necessary) and pipette a 5 ml aliquot into another 100 ml beaker. Add 20 ml plus or minus 0.5 ml of fresh Eriochrome cyanine solution ("Working solution") from a burette to the aliquot. Then add a few drops of acetic acid to remove the blue colour and give a clear red coloured solution. Dilute to 100 ml in a graduated flask and measure this colour using a colorimeter or a spectrophotometer.

Reagents

Nitric acid: concentrated sp.gr. 1.42.
Sodium hydroxide: 20% solution.
Acetic acid: concentrated.
Eriochrome Cyanine RC: Stock solution - 0.025%.
Working solution - 0.005%

Notes

1. A blank containing 1 g of H.C. copper must be included with each series of determinations.
2. The colour measurement should be made just after fifteen minutes standing.
3. The colour of the working solution of Eriochrome cyanine fades on standing so that only sufficient solution for the series of determinations should be made from the stock solution. A few ml of sodium hydroxide solution added to the "Working solution" increases the stability of the dilute solution.

Comparison of this colorimetric method was made with 150 gravimetric aluminium determinations as Al_2O_3 in 2% aluminium brasses.

All impurities in the Al_2O_3 were allowed for and were determined spectrographically. The greatest deviation in the 150 determinations was 0.01 per cent of the aluminium present in the alloy.

The maximum absorption of the aluminium-Eriochrome cyanine colour occurs at a wavelength of 550 mμ and a well defined transmittance curve is obtained. The colour system obeys the Beer-Lambert law.

Lead, zinc, tin and nickel do not interfere. Magnesium forms a red colour similar to that of aluminium; iron forms a red colour and copper gives a violet colour and a precipitate when the copper is in high concentrations; arsenic has a very slight effect. However the procedure of the method removes all these interfering elements by the treatment with sodium hydroxide.

SUMMARY

Aluminium is determined colorimetrically using Eriochrome cyanine. The application in this paper is to copper-aluminium alloys. The red colour obeys the Beer-Lambert law and the maximum absorption is at a wavelength of 550 mμ

RÉSUMÉ

L'aluminium peut être dosé colorimétriquement au moyen d'Ériochrome-cyanine. Les auteurs ont appliqué cette méthode aux alliages cuivre-aluminium. La coloration rouge obtenue obéit à la loi de Beer-Lambert; l'absorption maximum est à 550 mμ.

ZUSAMMENFASSUNG

Aluminium kann kolorimetrisch mit Eriochromcyanin bestimmt werden. In dieser Arbeit wird das Verfahren zur Analyse von Kupfer-Aluminium-Legierungen angewendet. Die rote Färbung folgt dem Beer-Lambertschen Gesetz; das Absorptionsmaximum liegt bei einer Wellenlänge von 550 mμ.

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SUR LE DOSAGE COLORIMÉTRIQUE DU FER

par

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Pour réduire Fe^{+3} en Fe^{+2} en vue du dosage colorimétrique de traces de ce métal, soit par l'*α.α'*-dipyridyle, soit par l'orthophénanthroline, on peut utiliser le chlorhydrate d'hydroxylamine, l'hydroquinone ou l'hydrosulfite de sodium.

Lorsque nous avons étudié le dosage colorimétrique du fer dans l'acide phosphorique et ses sels et établi, ensuite, une méthode basée sur le développement d'une teinte sensible[1,2], nous avons été amenée à faire choix de l'hydrosulfite de sodium qui s'était révélé comme étant l'agent de réduction le plus actif et par conséquent le plus sûr.

Cependant, l'hydrosulfite présente l'inconvénient de donner un dépôt de soufre lorsqu'il se trouve en trop grand excès; de plus, dans la méthode de la teinte sensible, il faut détruire l'excès par une ébullition prolongée.

Nous avons pensé que l'hypophosphite de sodium, réducteur énergique, ne présentant pas les inconvénients de l'hydrosulfite, pourrait lui être substitué. Pour nous en assurer nous avons repris nos essais en réduisant Fe^{+3} par l'hypophosphite de sodium et constaté que la réduction étant plus rapide à chaud qu'à froid, il y avait intérêt à l'effectuer vers 80°.

L'hypophosphite de sodium ne réduisant ni le bleu de méthylène, ni l'indigo est utilisable pour la méthode à la teinte sensible, dont le mode opératoire se trouve simplifié par son emploi.

Les modes opératoires que nous avons indiqués précédemment restent inchangés, la réduction de Fe^{+3} étant effectuée, vers 80°, par l'addition de 5 ml d'une solution d'hypophosphite de sodium pur à 20%.

Tout le fer est amené à l'état de Fe^{+2} en quelques minutes et l'excès d'hypophosphite est suffisant pour le préserver de toute oxydation pendant le refroidissement et les manipulations.

RÉSUMÉ

L'hypophospite de sodium est proposé pour la réduction de Fe^{+3} lors du dosage colorimétrique du fer au moyen de l'*α.α'*-dipyridyle et de l'orthophénanthroline.

SUMMARY

Sodium hypophosphite is proposed as a reducing agent for Fe^{+3} in the colorimetric determination of iron by *α.α'*-bipyridyl and by *o*-phenanthroline.

ZUSAMMENFASSUNG

Natriumhypophosphit wird zur Reduktion von Fe^{+3} bei der kolorimetrischen Bestimmung von Eisen mit *α.α'*-Bipyridyl oder *o*-Phenantrolin vorgeschlagen.

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COLORIMETRIC DETERMINATION OF MANGANESE

by

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The usual method applied for the colorimetric determination of manganese depends upon development of the pink permanganate colour. Oxidation is done by persulphate, bismuthate or periodate. Another extremely sensitive test makes use of formaldoxime hydrochloride. The latter method has received some attention during recent years mainly in application to biological work[1].

In this investigation use is made of the colour developed when freshly formed manganese dioxide dissolves in alkaline tellurate solution. The compound which forms is orange in dilute and dark red in concentrated solutions. This product of unknown constitution is usually met with in titrations involving alkaline permanganate[2] in the presence of telluric acid and was recently applied to the volumetric determination of manganese[3]. In that communication it was inferred that the colour is suitable for the colorimetric estimation of manganese[3] since it was observed that the depth of the colour varied with the amount of manganese used. The aim of the present work, is to confirm this prediction.

The method under hand possesses the advantage that the oxidation of manganese and the consequent development of colour take place easily and rapidly. Oxidation of manganese proceeds only to quadrivalent manganese and the method appears to be more suitable than the permanganate method for the determination of manganese in biological fluids containing reducing organic materials (to be published later).

EXPERIMENTAL

Reagents

1. *Manganese solution*

A $0.0943M$ solution of bivalent manganese was prepared by dissolving manganous sulphate in distilled water containing $0.1N$ sulphuric acid. The manganese content of the solution was determined volumetrically by the manganese(IV) tellurate method[3]. From this other solutions of lower concentrations were prepared by appropriate dilution.

2. *Telluric acid solution*

0.1 and $0.4M$ solutions were prepared by dissolving 1.92 and 7.68 g of the solid in 100 ml water.

3. *Other reagents used*

1 vol. hydrogen peroxide,

$5N$ sodium hydroxide.

The hydrogen peroxide solution was prepared by diluting a 20-vol. solution and its strength determined by titration with potassium permanganate.

Procedure of analysis

In the previous method for the volumetric estimation of manganese[3], the compound was prepared by adding 80 mg telluric acid per 5 mg of manganese. This was followed by sodium hydroxide sufficient to make the solution 2.5*N* and then 0.2 ml of 20-vol. hydrogen peroxide. This solution was shaken till it became clear and then heated to 60°C for about 10 minutes, followed by boiling to remove excess hydrogen peroxide, a process which led frequently to the deposition of a brick red precipitate which makes this procedure unsuitable for the colorimetric measurements. However, it is necessary to get rid of the excess H_2O_2 as otherwise its decomposition in alkaline solution leads to the evolution of oxygen bubbles which affect the results. The difficulty is overcome both for volumetric and colorimetric purposes by adding the quantity of hydrogen peroxide just necessary to oxidize the bivalent manganese to the quadrivalent state as calculated from the equation:

$$Mn(OH)_2 + H_2O_2 \rightarrow MnO_2 + 2\ H_2O$$

Under these conditions it is sufficient to heat the reaction mixture on a water bath at 60°C for $\sim$ 10 minutes to enhance development of the colour. If the procedure is performed properly, the solution remains clear.

Take 1 to 14 ml of 0.004715*M* manganese solution in a 25 ml measuring flask and mix with 4 moles of telluric acid per mole Mn(II). Add sufficient sodium hydroxide to make the solution 2.5*N* with respect to alkali. Add then the calculated amount of H_2O_2 solution, shake well and make up to the mark. Place in a clean dry Erlenmeyer flask and heat to 60°C for $\sim$ 10 minutes. The colour developed is then measured by a suitable instrument. In this investigation we operated on a Medico colorimeter, a Spekker photoelectric photometer (using a 1-cm cell) and a Beckman spectrophotometer. With the two former apparatus we used a blue filter and worked on solutions of concentrations varying from $1.886 \cdot 10^{-4}$ - $2.64 \cdot 10^{-3}M$. With the Beckman spectrophotometer we limited our measurements to the concentration range $1.886 \cdot 10^{-4}$ - $7.5 \cdot 10^{-4}M$ and operated at wavelengths of 400 and 420 Å.

RESULTS

The results obtained by the Medico colorimeter and the Spekker photometer are represented graphically in Fig. 1. These curves (% light absorbed *vs* the volume of Mn(II) solution) are only linear within the concentration range $1.886 \cdot 10^{-4}$ - $7.54 \cdot 10^{-4}M$. Above the latter concentration all the points lie on a smooth curve. From these results it is clear that the colour obeys Beer's law only within the concentration range $1.886 \cdot 10^{-4}$ - $7.54 \cdot 10^{-4}M$. The results obtained by the Medico colorimeter within this range are not sufficiently accurate for quantitative measurements. Better results are obtained by the use of the Spekker photometer and the Beckmann spectrophotometer. With the latter apparatus, the results obtained within the concentration range $1.886 \cdot 10^{-4}$ - $7.54 \cdot 10^{-4}M$ are shown in Fig. 2. From the two curves it is apparent that a better linearity is obtained at a wavelength of 420 Å. In Table 1 are shown the concentration of manganese in mg/litre together with the corresponding optical density. From these results it is concluded

TABLE I

ml 0.00472M Mn(II) solution used made up to 25 ml	*Concentration in mg/litre after dilution*	*Optical density*	
		at 420 Å	*at 400 Å*
1	10.359	0.087	0.13
2	20.718	0.190	0.28
3	31.077	0.273	0.40
4	41.436	0.371	0.53
5	51.495	0.430	0.6

that although the colour obeys Beer's law within a limited range of concentration yet by constructing calibration curves such as those shown in Fig. 1, the practicable concentration range can be extended to $2.64 \cdot 10^{-3} M$ Mn(II) with an error of ±1%.

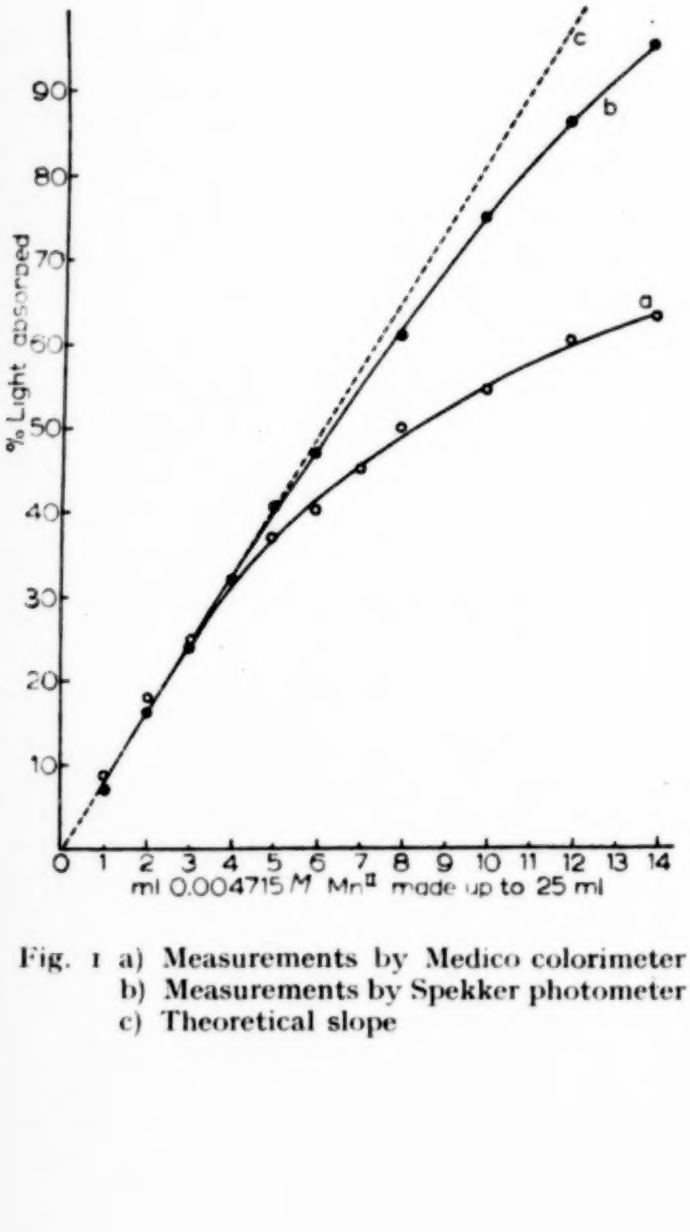

Fig. 1 a) Measurements by Medico colorimeter
b) Measurements by Spekker photometer
c) Theoretical slope

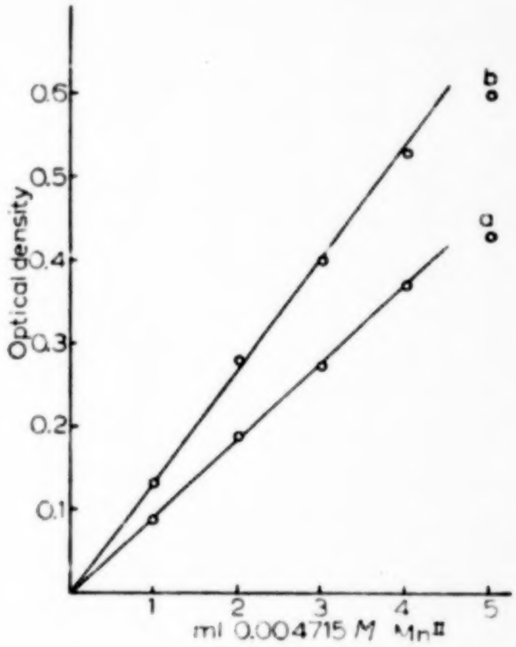

Fig. 2 Measurements by Beckman spectrophotometer
a) at 420° Å, b) at 400° Å

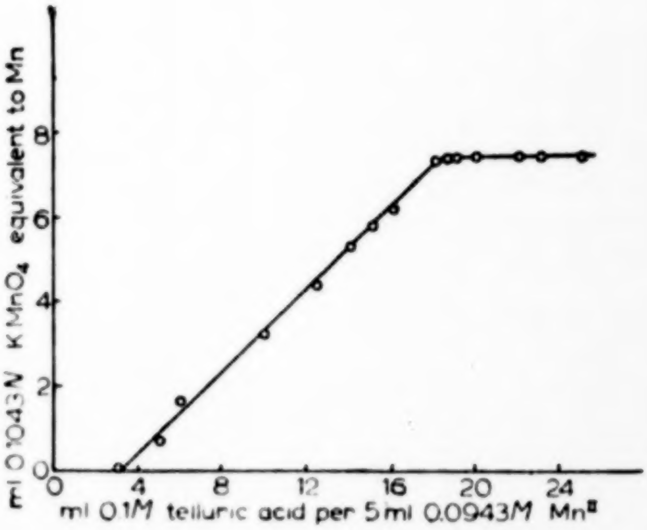

Fig. 3

Effect of concentration of the reagents on the colour intensity

a) Variation of alkali concentration between 1 and 2.5N does not affect the colour intensity.

b) By changing the telluric acid concentration so that no precipitation occurs, *i.e.* around the ratio Mn(II) : Te(VI) = 1:4, the colour is only slightly affected.

Precipitation might arise both when telluric acid is present in excess and in an amount less than sufficient to form the compound, *i.e.* Mn(IV) : Te(VI) = 1:4. If excess telluric acid is present, insoluble tellurate comes down as a crystalline solid occluding some of the red coloured compound. If on the other hand telluric acid is deficient, MnO_2 separates out giving rise to a turbid solution. In both cases erroneous results are obtained.

c) The excess hydrogen peroxide does not apparently cause any effect on the colour but a long time should elapse before the measurements are made until the oxygen bubbles are completely evolved.

Composition of the manganese(IV)- telluric compound

In determining the constitution of the coloured compound, 5 ml of 0.0943 *M* manganous solution were treated with increasing volumes of 0.1 *M* telluric acid together with the requisite amount of alkali to make the solution 2.5 *N* in sodium hydroxide and the equivalent amount of hydrogen peroxide. The solution was filtered through a 1 G4 sintered glass funnel and in the filtrate quadrivalent manganese was determined volumetrically[3]. The curve obtained by plotting the manganese concentration in the filtrate in moles against moles of telluric acid added is shown in Fig. 3.

From the curve it is clear that the manganese concentration in the filtrate becomes constant when 18.6 ml or more of 0.1 *M* telluric acid is present in the solution. The number of moles of telluric acid present in this volume is $\frac{18.6}{1000} \times 0.1 = 0.00186$ as compared with $\frac{5}{1000} \times 0.0943 = 0.0004715$ mols manganese. These data give a ratio of 1:4 for quadrivalent manganese to tellurate in the compound.

SUMMARY

The colour developed, when freshly formed manganese dioxide dissolves in alkaline tellurate solution is found to be suitable for the colorimetric determination of manganese. The colour obeys Beer's law within the concentration range $1.886 \cdot 10^{-4}$ - $7.54 \cdot 10^{-4} M$. The colour is developed by oxidizing Mn(II) (in presence of 2.5 *M* alkali) with the equivalent amount of H_2O_2 in the presence of 4 moles of telluric acid per mole Mn(II).

RÉSUMÉ

La coloration obtenue par dissolution du dioxyde de manganèse, fraîchement précipité, dans la solution d'un tellurate alcalin, peut être utilisée pour doser colorimétriquement le manganèse. Cette coloration obéit à la loi de Beer dans les limites de concentrations de $1.886 \cdot 10^{-4}$ à $7.54 \cdot 10^{-4} M$. L'oxydation de Mn^{+2} est effectuée, par une quantité équivalente de peroxyde d'hydrogène, en présence d'un hydroxyde alcalin 2.5 *M* et d'acide tellurique (4 molécules pour 1 Mn).

ZUSAMMENFASSUNG

Die Farbe welche sich entwickelt, wenn man frisch gefälltes Mangandioxyd in einer alkalischen Telluratlösung auflöst kann zur kolorimetrischen Bestimmung des Mangans herangezogen werden. Die Farbe folgt dem Beer'schen Gesetz innerhalb des Konzentrationsbereiches $1.886 \cdot 10^{-4}$-$7.54 \cdot 10^{-4} M$. Die Farbe wird entwickelt, indem man Mn (in Gegenwart von 2.5 *M* Alkali) mit der entsprechenden Menge H_2O_2 in Gegenwart von 4 Mol Tellursäure für je 1 Mol Mn oxydiert.

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SPECTROPHOTOMETRIC DETERMINATION OF MAGNESIUM WITH 1-AZO-2-HYDROXY-3-(2.4-DIMETHYLCARBOXANILIDO)-NAPHTHALENE-1'-(2-HYDROXYBENZENE)

by

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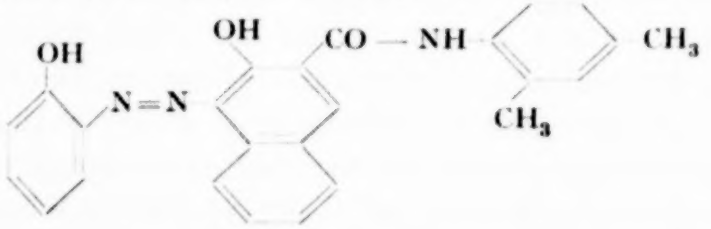
Direct colorimetric methods for determination of small quantities of magnesium generally involve adsorption of a dyestuff on the surface of colloidal magnesium hydroxide to form a color lake. The most widely used reagent of this type is Titan Yellow[1]. Colorimetric methods based on formation of soluble colored compounds are generally more satisfactory than those utilizing color lake formation because they are ordinarily less subject to error due to changes of conditions. Procedures have been described recently which utilize the formation of a colored complex compound of magnesium with Eriochrome Black T[2,3] and with sodium 1-azo-2-hydroxy-3-(2.4-dimethylcarboxanilido)-naphthalene-1'-(2-hydroxybenzene-5-sulfonate)[4]. This paper describes a method based on the use of 1-azo-2-hydroxy-3-(2.4-dimethylcarboxanilido)-naphthalene-1'-(2-hydroxybenzene) as a reagent.



This compound is similar in structure, properties and method of application to the sulfonic acid compound mentioned above. It does, however, differ from the sulfonic acid compound in being easier to synthesize. The method based on its use has a greater tolerance for water and for the presence of calcium ion. In addition, it has been found that maximum color development occurs immediately on preparation of solutions.

APPARATUS AND REAGENTS

Spectrophotometers. Beckman spectrophotometers, Model DK-2, with 1 cm silica cells and Model D, with 1 cm Corex cells were used.

Standard magnesium solution. The standard magnesium solution was prepared from reagent grade magnesium oxide. A sample of the ignited oxide (800-820°) weighing 1.658 grams was dissolved so as to obtain one liter of solution 0.1 *N* in hydrochloric acid and containing 1.00 mg of magnesium per ml. This solution was standardized gravimetrically by the oxine method and was stored in a polyethylene bottle.

Buffer solution. The buffer was prepared by dissolving reagent grade borax in water to give a 0.08*M* solution.

Reagent solution. The reagent solution was prepared by dissolving the compound in 95% ethanol to give a solution containing 0.10 mg/ml. The compound may be obtained from the La Motte Chemical Products Co., Chestertown, Md. (U.S.A.).

Other reagents. All other reagents were analytical grade and were used without further purification.

PROCEDURE

Transfer a 5 ml aliquot of the reagent solution to a 25 ml volumetric flask; add to this an aliquot containing 0.5 to 10 γ of magnesium in 2 to 15 ml of solution which has been adjusted so as to be just acid to phenolphthalein. Add 0.5 ml of 0.08*M* borax solution, make up to the mark with 95% ethanol and mix. Measure the absorbance at 505 mμ, using a distilled water blank. Determine the weight or concentration of magnesium in the unknown from a working curve prepared by this procedure using known amounts of magnesium.

For best results, it is desirable to prepare a new working curve with each freshly prepared reagent solution. Maximum precision will not be obtained at the lower extremity of the working curve; hence it is desirable to adjust the size of the magnesium aliquot to give 1 to 10 γ of magnesium for each determination.

PROPERTIES OF THE REAGENT

1-Azo-2-hydroxy-3-(2.4-dimethylcarboxanilido)-naphthalene-1′-(2-hydroxybenzene) is a red solid essentially insoluble in water, but soluble in many organic liquids. The material used in this investigation was synthesized for this purpose. On purification, a product was obtained which melted at 246-7°. Theoretical composition: C, 73.02; H, 5.11. Analysis: C, 72.98; H, 4.89. The compound may be dried at 100° and is believed to be stable at room temperature indefinitely. Ethanolic solutions are stable for at least two months. Because of the insolubility of this compound in water, all work described involved solutions of the compound in mixtures of water and ethanol. Acidic ethanolic solutions of the compound are red, while neutral or weakly basic solutions are blue. The color is red in strongly basic solutions. It was found that addition of borax, which would buffer an aqueous solution at pH 8.95, produces the blue form of the compound in ethanolic solution. Addition of magnesium ion under these conditions causes a color change from blue to salmon pink.

The absorption spectra of these two systems are shown in Fig. 1. It may be seen that the blue form of the reagent exhibits an absorbance maximum at 620 mμ, while in the presence of magnesium two maxima are observed, at 505 and 535 mμ, respectively. Under the conditions of the determination, the absorbance at 505 mμ is proportional to magnesium concentration. The spectra of Fig. 1 show that while the absorbance peak of the reagent overlaps that of the magnesium complex, the reverse is not the case. If an excess of reagent is present, the absorbance at 505 mμ is, therefore, the sum of the absorbances of the complex and of the excess reagent, whereas the absorbance at 620 mμ is caused by the presence of unreacted reagent only. The absorbance of excess reagent at 505 mμ is easily calculated because there is a proportional relationship between the absorbance of the reagent at 505 mμ and at 620 mμ. This value may then be deducted from the total absorbance at 505 mμ, leaving the absorbance due to the magnesium complex[5]. A calibration curve prepared by plotting absorbance at 505 mμ versus absorbance at 620 mμ for solutions containing varying concentrations of reagent but no magnesium is useful for making this correction. Absorbances of solutions in which magnesium is to be determined are measured at both wavelengths and the correction read from the calibration curve.

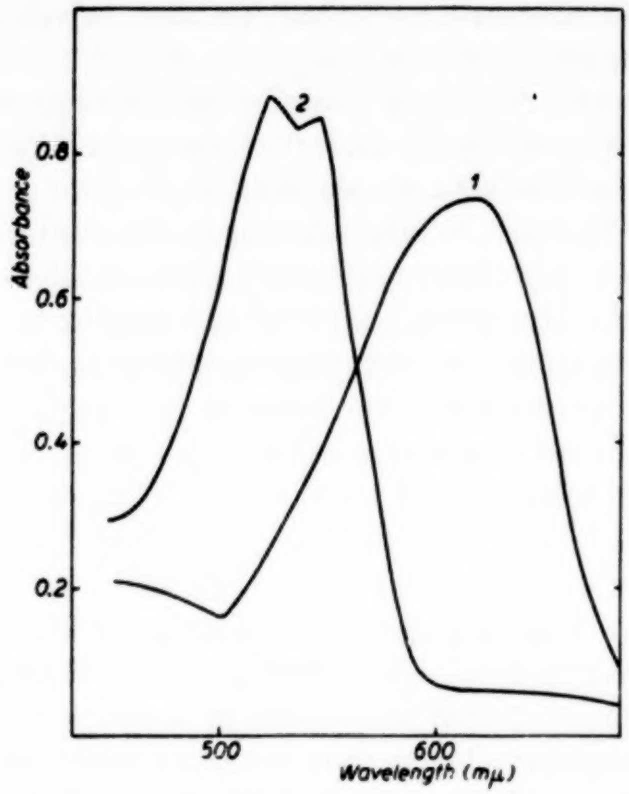


Fig. 1. Absorption spectra of reagent and its magnesium complex.
1. 20 p.p.m. of reagent.
2. 20 p.p.m. of reagent plus 40 p.p.m. of magnesium.

As stated above, there is a linear relationship between total absorbance at 505 mμ and the magnesium concentration. This relationship holds up to 0.4 p.p.m. of magnesium, but the curve does not pass through the origin of the graph. In addition, it will be shown that the precision obtained from measurements of total absorbance at 505 mμ is not significantly different from that of measurements which have been corrected for absorbance of unreacted reagent. The practice of making the correction does, however, eliminate small errors that are introduced if the reagent stock solution is prepared by weighing the solid on an ordinary analytical balance. These errors are appreciable since the weight of reagent needed is small (50 mg for 500 ml of stock solution). The necessity for making this correction may be avoided by preparing a new working curve for each fresh batch of reagent stock solution used.

OPTIMUM CONDITIONS

Effect of water

In the procedure for determination of magnesium recommended above, an aliquot of 2 to 15 ml of solution containing magnesium is specified. A lower limit is noted in order to prevent the precipitation of the borax buffer, which has limited solubility in ethanol. In the absence of an aliquot of solution to be tested, two ml of water will do as well. For this reason, it is not possible to increase the concentration of the buffer above that specified. If the solution to be analysed contains a high concentration of acid, it is necessary to adjust so as to be just acid to phenolphthalein. The small amount of acid thus introduced will not exhaust the capacity of the borax buffer. The adjustment is conveniently performed in the flask to be used for the determination. The aliquot of reagent and buffer can then be added, since the order of addition of components has no effect.

The upper limit on the amount of water added is necessitated by the limited solubility of the reagent and by the fact that the color exhibited by the reagent is in part dependent upon the concentration of water. Under the stated conditions the color of the reagent is blue; if however, the water content of the system is increased, the color changes quite sharply to violet when about 70% of water is present. This causes a shift in the absorbance peak of the reagent to shorter wavelengths, close to that of the magnesium complex, thus vitiating the determination. The color is independent of water content within the range of 19 to 70% water. This corresponds to the addition of 2 to 15 ml of aqueous solution per 25 ml in addition to the water furnished by the buffer solution and by the 95% ethanol.

Effect of time

No appreciable change in absorbance occurs during the first hour after preparation of solutions. Over a period of three days a fading of color corresponding to a decrease of 2.0% of the magnesium content was noted in a solution containing 0.40 p.p.m. of magnesium. Since this change is less than the error which must be expected for this measurement, the system is for practical purposes stable for at least three days.

Effect of temperature

The greater part of the absorbance data reported here were obtained using a spectrophotometer that did not have a water-jacketed cell compartment. It was, therefore, impossible to control the temperature at which these measurements were taken, though it was noted that cells left in the compartment more than a few moments became noticably warm to the touch. No appreciable change in absorbance was noted when solutions that had been allowed to equilibrate with the ambient temperature (24°) were heated in the cell compartment.

Effect of change in reagent concentration

If the total absorbance at 505 mμ is taken as a measure of magnesium concentration, it will of course be necessary to control rigidly the amount of reagent added. If, on the other hand, the correction for absorbance by unreacted reagent is made, it is only necessary to add sufficient reagent to react completely with the magnesium present, together with a large enough excess to force the reaction to completion. It was found that approximately 20 p.p.m. of reagent is necessary to force the reaction with 0.4 p.p.m. of magnesium to completion (three-fold molar excess of reagent). Decreasing the reagent concentration from 20 to 16 p.p.m. with the magnesium concentration held constant at 0.4 p.p.m. results in a relative decrease in absorbance of 6.2%. This is a significant change, since the relative standard deviation for this measurement is 2.3%. Further lowering of the reagent concentration causes a much larger decrease in complex absorption. This, together with the fact that the Beer's law relationship fails above 0.4 p.p.m. of magnesium, indicates that a reagent concentration higher than 20 p.p.m. would increase the range of the method. However, choice of an optimum concentration must take into consideration several other factors. The recommended stock solution or reagent (0.10 mg/ml) must be heated to achieve complete solution in a reasonable time. A more concentrated stock solution would be difficult to prepare; therefore to increase the reagent concentration a larger aliquot of stock solution would be necessary. This, of necessity, decreases the size of the aqueous aliquot that can be added, thus decreasing the actual sensitivity of the method. In addition, the maximum absorbance encountered in the recommended procedure is approximately 0.840 absorbance unit, slightly above the optimum range for spectrophotometric measurements. In consideration of these factors, a 20 p.p.m. reagent concentration achieved by addition of a 5 ml aliquot of 0.10 mg/ml stock solution is recommended.

Effect of other metals

The effect of addition of Fe^{+2}, Fe^{+3}, Cu^{+2}, Al^{+3}, Sr^{+2} and Ca^{+2} on the determination was checked. It was found that Fe^{+2}, Fe^{+3}, Cu^{+2} and Al^{+3} react with the reagent and cause substantial interference when present only to the extent of 1 p.p.m. Ca^{+2} and Sr^{+2} on the other hand, do not form colored complexes with the reagent and interfere only when they are present in sufficient concentration to be insoluble in the alcoholic medium. Tolerance of the method for alkaline earth ions will depend upon the identities and concentrations of anions present and the amount of water in the system. For determinations containing 30% of water and only borate and chloride, the tolerance is approximately 20 p.p.m. for both Ca and Sr.

When this method of determination is applied to analysis of complex mixtures, it is anticipated that heavy metals, when present in concentrations of the same order of magnitude as that of magnesium or larger, will have to be removed. The authors have found the technique of chloroform extraction with 8-quinolinol to be a convenient one for removal of many heavy metals when they are present to the extent of one milligram or less[4].

PRECISION, SENSITIVITY AND RANGE OF THE METHOD

To check the precision of the method, series of twelve replicate determinations were made with 0.040, 0.20 and 0.40 p.p.m. of magnesium, respectively. The results of these determinations were calculated both with and without the correction for absorption at 505 mμ by excess reagent and are shown in Tables I and II. It may be seen from these data that the method of handling results makes no significant difference in the precision.

TABLE I

PRECISION OF DETERMINATION

Magnesium concentration p.p.m.	*Absorbance 505 mμ*	*Standard deviation from the mean*	
		Absolute absorbance units	*Relative % of Mg presents*
0.040	0.341	0.003	7.5
0.20	0.488	0.008	4.0
0.40	0.665	0.009	2.2

TABLE II

PRECISION OF DETERMINATION

Magnesium concentration p.p.m.	*Absorbance* 505 mμ*	*Standard deviation from the mean*	
		Absolute absorbance units	*Relative % of Mg present*
0.040	0.038	0.005	9.0
0.20	0.268	0.010	3.6
0.40	0.538	0.013	2.3

* Data corrected for absorption by excess reagent.

The spectrophotometric sensitivity of this method is 0.00075 γ per sq.cm. For comparison the recorded sensitivities of other methods are: Titan Yellow, 0.006 γ; quinalizarin, 0.017 γ; Brilliant Yellow, 0.02 γ[6] and sodium 1-azo-2-hydroxy-3-(2.4-dimethylcarboxanilido)-naphthalene-1′-(2-hydroxybenzene-5-sulfonate), 0.0008 γ[4]. The practical sensitivity of the new reagent may be taken as 1 part of magnesium in 50,000,000 parts of solution. Solutions containing this concentration will have absorbances that are about 0.020 unit greater than those of solutions which contain no magnesium.

Beer's law is obeyed up to 0.4 p.p.m. of magnesium; the range of applicability of the method is 0.02 to 0.4 p.p.m. The concentration range for optimum precision is 0.1 to 0.4 p.p.m. of magnesium.

SUMMARY

1-Azo-2-hydroxy-3-(2.4-dimethylcarboxanilido)-naphthalene-1′-(2-hydroxybenzene) is recommended as a new reagent for the spectrophotometric determination of small quantities of magnesium. Optimum conditions for the determination have been outlined; data concerning the precision, sensitivity, range and effect of diverse ions are presented.

RÉSUMÉ

Le 1-azo-2-hydroxy-3-(2,4-diméthylcarboxanilido)-naphtalène-1′-(2-hydroxybenzène) est recommandé comme réactif nouveau pour le dosage spectrophotométrique de faibles quantités de magnésium. Les conditions optimums pour ce dosage ont été établies; des données concernant la précision, la sensibilité, les concentrations utilisables et l'effet de divers ions sont exposées.

ZUSAMMENFASSUNG

1-Azo-2-hydroxy-3-(2.4-dimethylcarboxanilido)-naphtalen-1′-(2-hydroxybenzol) wird als ein neues Reagenz zur spektrophotometrischen Bestimmung von kleinen Magnesiummengen empfohlen. Die besten Bedingungen zur Ausführung der Bestimmung werden umschrieben; Angaben über Genauigkeit, Empfindlichkeit, Anwendbarkeit, und Wirkung verschiedener Ionen werden mitgeteilt.

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DETERMINATION OF SODIUM IN ALUMINIUM-COPPER ALLOYS USING THE FLAME PHOTOMETER

by

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In a recent paper* by the authors, a flame photometric method of determining sodium in plain aluminium was described. The method has now been extended to the analysis of aluminium-copper alloys.

Although both copper and aluminium modified the intensity of the sodium flame for a given concentration of sodium, it was found possible to make up calibration curves for a given alloy from which the sodium content of a solution would be calculated.

EXPERIMENTAL

In order to avoid unnecessary experimental work it was assumed that the final method would involve dissolving 1 g of aluminium alloy, centrifuging if necessary and adjusting the volume to 100 ml. In this way the total concentration of aluminium and copper in the test solution cannot exceed one per cent and normally the copper percentage will be considerably less than this.

However, for completeness, greater concentrations of aluminium and copper were examined. In this case solutions of copper were taken and passed through the flame photometer with the sodium filter in position. It was found that with increasing copper concentration, there was an increase in the instrument reading showing an apparent increase in sodium concentration.

Aluminium was then added to these solutions and the apparent sodium content decreased showing a balancing of errors. These observations were recorded, but since these phenomena occurred at a concentration greater than those anticipated in the final procedure, further experimental work to find an explanation was considered to be outside the scope of the work.

Confining the total aluminium and copper concentrations to one per cent, a number of series of solutions were made up in which the copper and aluminium concentrations were constant and the sodium concentration was varied. In each individual series the copper concentration was varied. The aluminium was maintained at the concentration expected when 1 g of alloy is dissolved up into 100 ml of solution. The results obtained were plotted and are shown below.

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* H. F. HOURIGAN AND J. W. ROBINSON, *Anal. Chim. Acta*, 13 (1955) 179.

RESULTS

Figure 1 summarizes the readings obtained on the flame photometer from solutions of varying sodium and copper concentrations in the presence of aluminium.

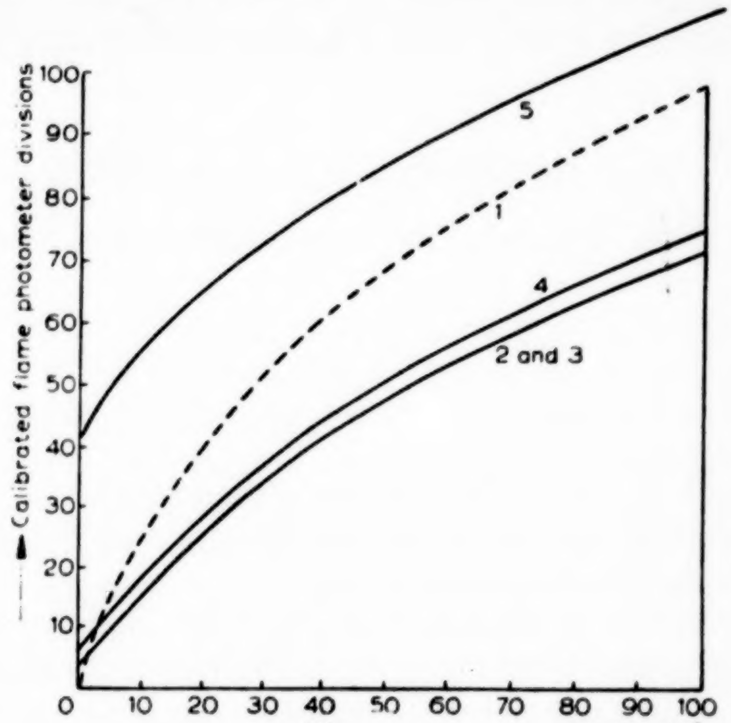

Fig. 1.

1 Cu 0.00% ; Al 0.00M ; Na 0-100 p.p.m.
2 Cu 0.00% ; Al 0.966M; Na 0-100 p.p.m.
3 Cu 0.045%; Al 0.966M; Na 0-100 p.p.m.
4 Cu 1.00% ; Al 0.966M; Na 0-100 p.p.m.
5 Cu 4.00% ; Al 0.966M; Na 0-100 p.p.m.
Total volume: 100 ml.

As can be seen, within the limits of concentration expected, *i.e.*, one per cent total metal, the copper concentration was not critical and it was found possible to make calibration curves from solutions where the aluminium and copper concentrations are similar to the solutions obtained from the alloy being examined.

For a four per cent copper in aluminium alloy, which is a common alloy, it is not necessary to know the copper content accurately before making up the calibration curve. This follows because curves two and three (Fig. 1) were not distinguishable showing that the same curve is suitable for any alloy containing less than four per cent copper. Curve four shows some displacement, but this corresponds to 100% copper and serves to illustrate the small effect of copper when the alloy is treated this way. Curves one and five are shown for completeness.

As a further check on the accuracy of the method, some available alloys were analysed by gravimetric precipitation of sodium with zinc uranyl acetate and were compared with the results obtained by this method. Typical results are shown below:

TABLE I

Sample	*Sodium content* *Gravimetric method* *p.p.m.*	*Flame photometric method* *p.p.m.*
1	2.5	2.6
2	3.3	3.2

As can be seen the agreement was reasonable.

As a further check, two samples of alloys were taken, dissolved and tested on the flame photometer. To each a known quantity of sodium solution was added from a hypodermic syringe to avoid significantly changing the volume of solution. The difference between the two readings on the photometer should be equivalent to the sodium added.

The results are listed in Table II below:

TABLE II

Sample	*Na^+ added p.p.m.*	*Na^+ expected p.p.m.*	*Na^+ found p.p.m.*
Alloy	Nil		2.5
Alloy	10	12.5	12.7
Alloy	50	52.5	53.5
Alloy	100	102.5	104.5

The results were considered reasonably accurate.

RECOMMENDED PROCEDURE

Briefly the principle of the method is as follows: 1 g of alloy is dissolved in hydrochloric acid. The volume of the filtrate is adjusted to 100 ml and any silica, *etc.*, left undissolved is centrifuged to the bottom of the solution. The clear supernatant liquid is then passed through a flame photometer in the normal way. The analysis of the alloys needs to be known approximately for making up calibration curves, the metallurgical alloy type is usually sufficient for this purpose since the copper and aluminium may vary several per cents without introducing significant error.

The procedure recommended is as follows:

Reagents

Sodium free water	
Hydrochloric acid	Concentrated pure reagent.
Aluminium	Spectrographically pure metal.
Copper	Spectrographically pure metal rods were dissolved in nitric acid, precipitated as the hydroxide, filtered and redissolved as with aluminium.
Sodium chloride	Dry AnalaR NaCl was weighed out and dissolved in sodium free water to give 10,000 p.p.m. of Na^+ 25.418 g NaCl = 10,000 p.p.m./litre.

Procedure

Dissolve 1 g of sample (drillings or turnings) in 15 ml concentrated hydrochloric acid using a 750 ml polythene beaker. Since the reaction is vigorous a smaller beaker may lead to the loss of some solution.

Adjust the volume to 100 ml with water, shake and allow the black precipitate of silicon to settle. If appreciable amounts of silicon are present it can be centrifuged to the bottom. This avoids filtering and the inherent danger of sodium pick up. Any error caused by varying amounts of silicon and its effect on the concentration of solution is small compared to the error of the instrument and can be ignored. This was verified experimentally.

The solution is then run through a flame photometer using a sodium filter. The intensity of the flame is measured using the calibration curve.

A blank must be run using 15 ml of concentrated hydrochloric acid and treating it exactly as the sample with reagents from the same bottle and subtracting the reading from the reading obtained on the sample in the normal way. Great care is necessary to ensure that all apparatus is clean and free from sodium ions before use.

Standardization curves

The percentage of aluminium, copper and silicon, if this is a major constituent of the alloy must be known approximately. A set of standards, each 100 ml, is made up containing 0, 10, 25, 50, 65, 85, 100 p.p.m. of sodium.

A litre of solution is then made up with the copper and aluminium concentration the same as that expected when 1 g of alloy is dissolved and made up to 100 ml of solution. Aliquots of this solution are then taken and the sodium content adjusted by adding NaCl solution by means of an hypodermic syringe. The series should contain respectively 0, 5, 10, 20, 40, 60, 80, 100 p.p.m. of sodium.

After thorough stirring, these solutions are photometered and a standard curve drawn from the results obtained.

CONCLUSIONS

The results indicate that the flame photometer can be used for the routine determination of sodium in aluminium copper alloys. Silicon does not interfere with the method which is rapid and reasonably accurate.

ACKNOWLEDGEMENTS

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SUMMARY

A flame photometric method of determining sodium in aluminium-copper alloys has been developed. Silicon and copper were found not to interfere. The method is rapid and reasonably accurate. It is designed for routine analysis.

RÉSUMÉ

Une méthode photométrique de flamme a été établie pour le dosage du sodium dans les alliages aluminium-cuivre. Le silicium et le cuivre ne gênent pas. Cette méthode est rapide et d'une bonne précision. Elle est recommandée à des analyses en série.

ZUSAMMENFASSUNG

Eine flammenphotometrische Methode zur Bestimmung von Natrium in Aluminium-Kupfer-Legierungen wurde entwickelt. Silizium und Kupfer stören nicht. Die Methode is rasch und ziemlich genau. Sie wird für Routineanalysen empfohlen.

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CURRENT EFFICIENCY AND TITRATION EFFICIENCY IN COULOMETRIC TITRATIONS WITH ELECTROGENERATED CERIC ION DETERMINATION OF IODIDE

by

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This study was originally initiated simply to determine the feasibility of titrating iodide ion with electrogenerated ceric ion. However, as the investigation progressed our interest was drawn to the general and fundamental question of the relation between overall titration efficiency and current efficiency in coulometric titrations with ceric ion.

Titration efficiency is measured by the agreement between the quantity of substance taken and the quantity found. If a considerable fraction of the substance undergoes direct reaction at the working electrode, so that only a minor fraction is titrated via the generated titrant, a relatively high titration efficiency can result even though the current efficiency for generation of the titrant falls short of 100%.

Electrogenerated ceric ion has been employed very successfully for the determination of various reductants, particularly by FURMAN and his co-workers[1-7]. However, surprisingly little is known about the current efficiency for ceric ion generation as distinct from titration efficiency. It is significant that all of the reductants successfully titrated (ferrous ion, ferrocyanide ion, +3 titanium, +4 uranium, +3 arsenic, hydroquinone, and *p*-methylaminophenol sulfate) are capable of direct oxidation at a platinum anode, so that 100% titration efficiency does not necessarily reflect 100% current efficiency for ceric ion generation. We have found that even under most optimum conditions the current efficiency for ceric ion generation is not better than about 99.8%, and at both very small and very large generating current densities it falls considerably below this figure. Consequently relatively large positive titration errors can result if the current density is either below or above the optimum range, especially when the substance being titrated is incapable of direct oxidation at the platinum generator anode.

EXPERIMENTAL TECHNIQUE

The coulometric titrations were performed in the usual manner[8]. The titration cell had a capacity of about 100 ml. For most of the experiments the generator anode was a platinum foil with an area of 3.1 cm^2, and the generator cathode was a coil of platinum wire separated from the test solution by immersion in a glass tube closed by a sintered glass disk. Efficient stirring was provided by a magnetic stirrer.

For potentiometric end-point indication the potential of a platinum indicator electrode in the test solution was measured in the ordinary fashion against a saturated calomel reference electrode.

The amperometric indicator circuit comprised a pair of bright platinum electrodes (area *ca.* 0.5 cm^2 each) across which a small constant voltage was applied from a radio type potentiometer powered by a 1.5 V dry cell. The indicator current was observed with a microammeter in series with the indicator electrodes.

Current-anode potential curves were obtained by imposing a voltage across the generator electrodes, and measuring the potential of the generator anode against a saturated calomel reference electrode with a potentiometer and the corresponding current with a milliammeter in series with the generating electrodes. Care was taken to wait a few minutes at each measurement point until the current had decayed to a steady value. The solutions were stirred efficiently by a magnetic stirrer, and the rate of stirring was kept as nearly constant as possible in the various trials. The current-anode potential curves were measured with the same cell and generator anode used for the coulometric titrations.

Some current-potential curves were also obtained with a platinum microelectrode in well stirred solutions by the usual polarographic recording technique.

CURRENT EFFICIENCY FOR GENERATION OF CERIC ION

The current efficiency for the electrogeneration of ceric ion by oxidation of cerous ion at a platinum anode in sulfuric and perchloric acid media can be estimated from the typical current-anode potential curves in Figs. 1 and 2. Fig. 2 is an enlarged scale plot of the lower sections of the curves of Fig. 1, and shows more clearly the ratio of the ceric and oxygen currents at the smallest current densities.

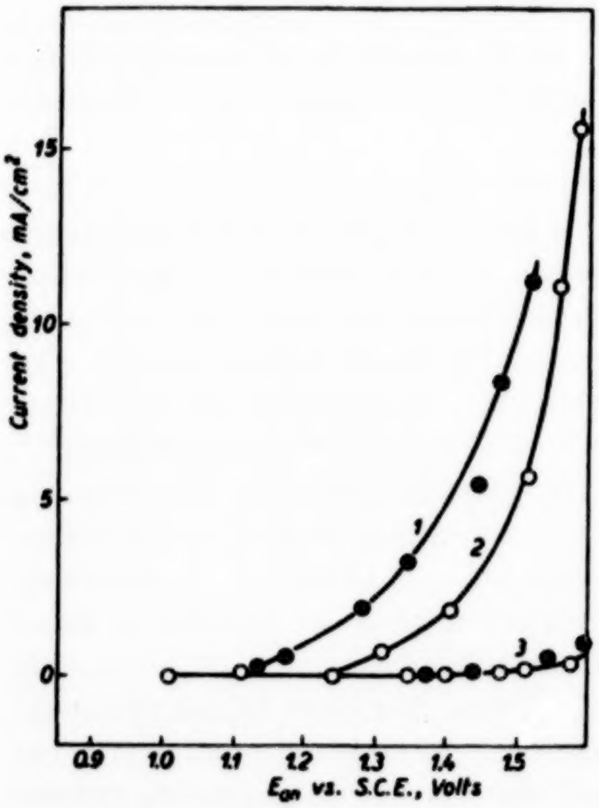

Fig. 1. Current-anode potential curves for oxidation of cerous ion.
1. 0.025 *F* cerous sulfate in 0.9 *F* sulfuric acid.
2. 0.05 *F* cerous perchlorate in 1 *F* perchloric acid.
3. 1 *F* perchloric acid or 0.9 *F* sulfuric acid alone.

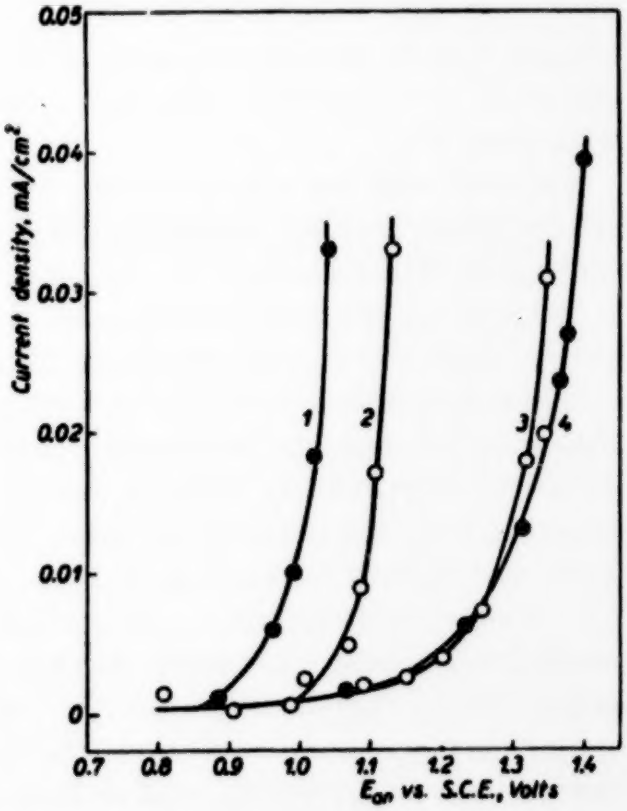

Fig. 2. Enlarged scale plots of the lower sections of the curves in Fig. 1.
1. 0.025 *F* cerous sulfate in 0.9 *F* sulfuric acid.
2. 0.05 *F* cerous perchlorate in 1 *F* perchloric acid.
3. 1 *F* perchloric acid alone.
4. 0.9 *F* sulfuric acid alone.

The current-potential curve for the oxidation of water to oxygen is essentially the same in perchloric and sulfuric acid solutions of the concentrations used in these experiments. However, the oxidation of +3 cerium occurs at a significantly smaller potential in sulfuric acid than in perchloric acid solution. This accords with the fact that the formal potential of the ceric-cerous couple is somewhat less oxidizing in sulfuric than in perchloric acid medium, probably because of complexation of ceric ion with hydrogen sulfate ion. It is evident that sulfuric acid solutions are much more conducive to high current efficiency for oxidation of cerous ion than are perchloric acid solutions.

Comparison of the curves in Figs. 1 and 2 with the formal potentials of the ceric-cerous couple (+1.46 V *vs.* S.C.E. in 1 *F* perchloric acid and +1.20 V *vs.* S.C.E. in 1 *F* sulfuric acid) indicates that in both media the overpotential is quite small, *i.e.*, the oxidation of cerous ion proceeds nearly reversibly. That the ceric-cerous couple in sulfuric acid media behaves nearly (although not perfectly) reversibly has been confirmed from composite anodic-cathodic current potential curves of mixtures of millimolar concentrations of ceric and cerous sulfates. Such curves pass through the zero current axis with no inflection, and the slopes of the cathodic and anodic sections are only about twice as large as the value expected for reversibility. The couple functions more reversibly the greater the sulfuric acid concentration up to at least 8 *F*. The cathodic and anodic sections both show well developed limiting currents.

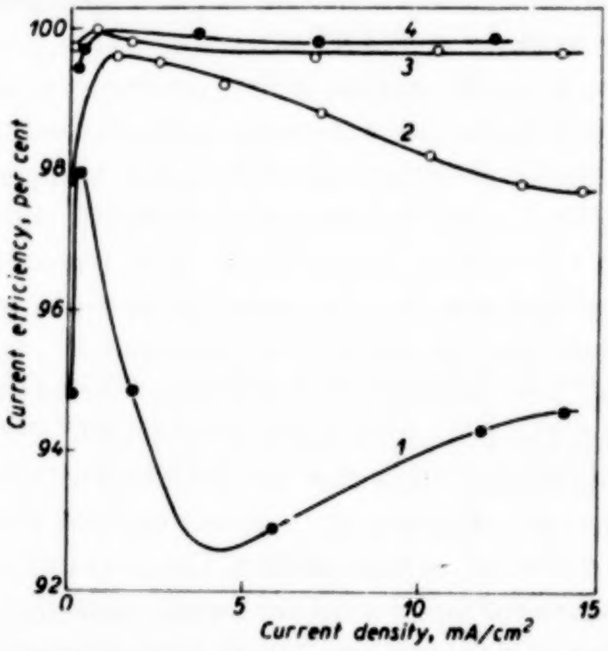

Fig. 3. Current efficiency for electrogeneration of ceric ion as a function of current density and solution composition.
1. 0.05 *F* cerous perchlorate in 1 *F* perchloric acid.
2. 0.025 *F* cerous sulfate in 0.9 *F* sulfuric acid.
3. 0.1 *F* cerous sulfate in 0.9 *F* sulfuric acid.
4. 0.1 *F* cerous sulfate in 3 *F* sulfuric acid.

At any selected potential in Figs. 1 and 2 the total current, i, is the sum of a contribution, i_{Ce}, resulting from oxidation of cerous ion and a contribution, i_O, from oxidation of water to oxygen and hydrogen ion, *i.e.*, $i = i_{Ce} + i_O$. If, at a given potential, the current from oxygen evolution is the same in the presence and absence of cerous ion, then the current efficiency for oxidation of cerous ion will be i_{Ce}/i or $(i - i_O)/i$. Although this condition need not be universally true it is satisfied in this case, because current efficiencies evaluated by a direct method described later on agree with those predicted from the current-anode potential curves.

Fig. 3 shows the current efficiencies, evaluated in terms of $(i - i_O)/i$ from current-potential curves, as a function of current density. The much better current efficiency in sulfuric than in perchloric acid is evident. Indeed, coulometric titrations in perchloric acid media can be expected to be successful only when a major fraction of the substance being determined undergoes direct reaction at the platinum anode. This condition can be satisfied only by selecting a generating current that is smaller than the limiting current for the direct electrooxidation of the substance being determined during most of the titration, but this is inimical to rapid practical titrations.

With 1 *F* sulfuric acid (curve 2 in Fig. 3) the current efficiency falls much below 100% both at very small and very large current densities, and the maximal current efficiency at intermediate current densities is still a few tenths of a percent short of 100%. With other conditions constant, the current efficiency is very greatly improved with increasing sulfuric acid concentration. With 3 *F* sulfuric acid (curve 4 in Fig. 3) the efficiency remains within a few tenths of a percent of 100% over a wide range of current densities. Current-anode potential curves of mixtures of ceric and cerous sulfates in 1 to 8 *F* sulfuric acid revealed two reasons for this beneficial effect of increasing sulfuric acid concentration. Firstly the ceric-cerous couple behaves more reversibly the higher the sulfuric acid concentration, and its formal potential becomes somewhat smaller, presumably because of complexation of ceric ion with hydrogen sulfate ion. Secondly, the potential of oxygen evolution becomes higher (more oxidizing) the greater the concentration of sulfuric acid. Both these effects operate to widen the potential range over which cerous ion can be oxidized without concomitant oxidation of water (or sulfate ion).

As expected, the current efficiency at a given current density is closer to 100% the larger the concentration of cerous sulfate. The maximal concentration of cerous ion that can be used is limited by the rather small solubility of cerous sulfate, which is about 0.15 *F* in water at 25° and smaller at higher temperatures.

The current efficiencies predicted by the current-potential curves were verified by coulometric titrations of iodide ion, both in the ordinary manner with the iodide present from the start and by generating about 95% of the requisite quantity of ceric ion before the iodide sample was added. In two such trials, at a current density of 16 mA/cm^2 with 0.06 *F* cerous sulfate in 1 *F* sulfuric acid, the time required to reach the end-point was 3.0% and 2.6% larger when most of the requisite ceric ion was generated before the iodide ion was added than when iodide ion was present from the start. The average current efficiency of 97.2% agrees with the value 97.7% predicted from curve 2 in Fig. 3 for the current density used (16 mA/cm^2).

In these trials, as well as in the many others described in a following section, the titration efficiency was within about 0.2% of 100% when the iodide sample was present from the start.

The cardinal factor governing the current efficiency is, of course, the potential adopted by the working electrode rather than current density, *i.e.*, current is the result and not the cause of an electrode reaction. We have referred current efficiency to current density simply as a practical expedient, since current density is always known in practical coulometric titrations and the potential of the working electrode ordinarily is not measured.

In predicting net titration efficiency from curves like those in Fig. 3 one must bear in mind that the pertinent current is that resulting from oxidation of cerous ion. This is smaller than the total generating current during most of the titration, to a degree dependent on the amount of direct electro-oxidation of iodide ion (*vide infra*). This tends to greatly improve the net titration efficiency at the higher current densities.

ADAMS, REILLEY AND FURMAN[1] imply that maximal current efficiency for ceric ion generation can be expected only at relatively small current densities, but this is certainly not true for very small current densities with the usual concentration of sulfuric acid of about 1 *F*. The large drop in current efficiency at current densities below about 1 mA/cm^2 is especially significant in titrations of microgram quantities, and it is probably responsible for the preponderance of positive errors evident in published titration efficiency data for ferrous ion, hydroquinone, +3 arsenic, and *p*-methylaminophenol sulfate obtained with very small generating currents. When microgram quantities of a substance are to be titrated with small generating currents the generator anode should have a commensurately small area, to maintain the current density above the minimum allowable value. If chemically and thermodynamically permissible, a relatively high (*e.g.* 3 *F* or greater) sulfuric acid concentration should also be used.

TITRATION EFFICIENCY IN TITRATIONS OF IODIDE ION AND FERROUS ION

Table I presents results of the coulometric titration of various amounts of iodide ion, using both potentiometric and amperometric end-point detection.

Potentiometric end-point detection, with a platinum indicator electrode and sa-

TABLE I

COULOMETRIC TITRATION OF IODIDE ION WITH ELECTROGENERATED CERIC ION

The supporting electrolyte (50 to 100 ml) was 0.025 *F* in $Ce_2(SO_4)_3$ and 0.9 *F* in sulfuric acid. Generating currents ranging from 7 to 60 mA (current densities 2 to 19 mA/cm^2) were used.

Iodide, mg		*Error*	*End-point*
Taken	*Found*	*%*	*detection*
31.59	31.74	+0.5	Potentiometric
	31.65	+0.2	,,
	31.62	+0.1	,,
	31.72	+0.4	,,
6.316	6.323	+0.1	,,
	6.346	+0.5	,,
6.278	6.228	−0.8	,,
5.175	5.217	+0.8	,,
	5.190	+0.3	,,
	5.168	−0.1	,,
31.58	31.60	+0.1	Amperometric
	31.55	−0.1	,,
	31.63	+0.2	,,
	31.49	−0.3	,,
5.175	5.184	+0.2	,,
	5.186	+0.2	,,
	5.170	−0.1	,,
	5.171	−0.1	,,
	5.173	0.0	,,
1.294	1.299	+0.4	,,
	1.294	0.0	,,
	1.289	−0.4	,,

turated calomel reference electrode, was performed in the usual, familiar manner. The characteristics of the potentiometric iodide-ceric titration curve are discussed in detail in Reference[8] (p. 116 *et seq.*).

A typical amperometric titration curve is shown in Fig. 4. This curve shows the change in current between two identical platinum indicator electrodes (area 0.5 cm^2 each) across which a small constant voltage (100 mV) was impressed.

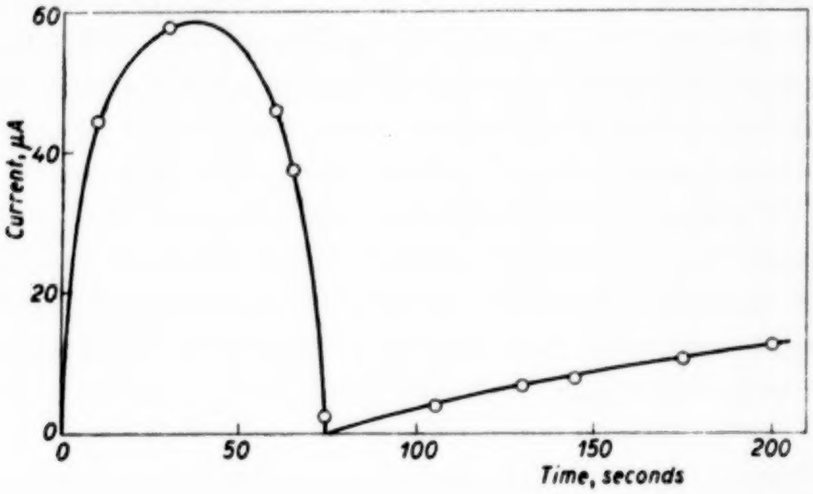

Fig. 4. Typical amperometric titration curve obtained with two polarized platinum electrodes in coulometric titration of iodide ion with ceric ion.

At the start of the titration the only possible reactions at the indicator electrodes are

$$2H^+ + 2e = H_2 \quad \text{(cathode)}$$
$$2I^- = I_2 + 2e \quad \text{(anode)}$$

but the impressed voltage used is too small to permit the indicator cathode potential to become reducing enough for reduction of hydrogen ion to occur, so the indicator current is very small. As soon as iodine is produced in the titration the cathode reaction becomes $I_2 + 2e = 2I^-$, and since this is just the reverse of the anode reaction the indicator electrode pair becomes equivalent to a "concentration cell" of zero decomposition voltage. Consequently the indicator current increases, and reaches a maximum about halfway through the titration. During the second half of the titration the current decreases due to the decreasing rate of depolarization of the indicator anode resulting from the decreasing iodide ion concentration.

When the equivalence point is reached the concentration of iodide ion is infinitesimally small, and the only possible reaction at the indicator anode is oxidation of cerous to ceric ion. However, with the small applied voltage used (and since the potential of the indicator cathode is poised at the potential of iodine reduction) the anode potential is not sufficiently oxidizing (positive) to cause oxidation of cerous ion at an appreciable rate, and the indicator current is very small.

Beyond the equivalence point, the excess ceric ion undergoes reduction (along with iodine) at the indicator cathode. This causes the potential of the indicator cathode to become more positive (less reducing). Since the applied voltage is constant, the potential of the indicator anode correspondingly also becomes more positive, and the rate of oxidation of cerous ion at it (and hence the current) increases.

The end-point was taken empirically as the intersection of the two branches of the curve near the equivalence point. Strictly, this intersection does not coincide exactly with the true equivalence point, but the good results obtained by its use demonstrate that the discrepancy is negligibly small.

With the largest quantities of iodide ion a generating current density of 13 mA/cm² was employed when potentiometric end-point detection was used, and in the trials with amperometric end-point detection the current density was as large as 19 mA/cm². From curve 2 in Fig. 3 the current efficiency for ceric ion generation is only 97 to 98% at these relatively large current densities. In spite of this poor generation efficiency the titration error averages only about ± 0.3%. On the other hand, when 95% of the requisite ceric ion was generated before the iodide sample was added the expected positive error of 2 to 3% was observed.

The small net titration error results from direct electrooxidation of iodide ion, but oxidation only to iodine cannot account entirely for the smallness of the error. Anodic polarization curves of iodide ion show a well defined limiting current for the oxidation of iodide ion to iodine. With the same cell and generator anode used for the coulometric titrations, the limiting current density for oxidation to iodine is approximately 2.0 mA/cm² for solution compositions corresponding to the largest iodide samples of Table I. Thus the current resulting from direct electro-oxidation to iodine is much too small a fraction of the total generating current at the largest current densities used (13 and 19 mA/cm²) to account for the small titration errors.

These data suggested that electro-oxidation of iodide ion proceeds above the elemental state, probably to iodate ion, at the potential adopted by the working anode. The iodate ion thus formed at the anode surface is stirred back into the solution where it oxidizes an equivalent quantity of iodide ion to iodine. The limiting current density for oxidation to iodate ion is six times that for oxidation to iodine, which means that under the conditions of the largest samples in Table I it would be about 12 mA/cm², and thus almost as great as the largest generating current densities used. Because the sum of the equivalent concentrations of iodide ion and iodine remain constant throughout the titration, the current resulting from oxidation of iodine to iodate ion remains constant and large. Consequently only a small fraction of the electricity corresponding to the net titration of iodide ion to iodine results from electrogeneration of ceric ion. In other words, a major fraction of the titration proceeds via electrogenerated iodate ion.

This interpretation was substantiated by performing titrations *without any cerous salt present*. When the generating current was slightly smaller than the limiting current for the oxidation of iodine to iodate ion (*i.e.*, smaller than six times the iodide ion to iodine limiting current) the quantity of electricity required to reach a potentiometric iodine end-point agreed to within a few parts per thousand with the theoretical value. When the selected generating current was larger than the iodine to iodate ion limiting current positive titration errors resulted, and their magnitude increased the more the iodate limiting current was exceeded, due to simultaneous oxidation of water.

KOLTHOFF AND JORDAN[9] studied the oxidation of iodide ion, and iodine, in dilute perchloric acid media at a rotated platinum microelectrode by the polarographic technique, and concluded that iodine was oxidized to hypoiodous acid. This conclusion was based solely on the observation that under the particular conditions that they employed (*e.g.*, rate of polarization) the iodine oxidation wave happened to have about the same height as an equivalent concentration of iodide ion. However, as KOLTHOFF AND JORDAN themselves demonstrated, the iodine oxidation wave in dilute perchloric acid does not display a really definite limiting current, and furthermore no wave at all is observed if the polarogram is recorded with decreasing polarization. Thus the current-anode potential curve does not provide reliable evidence for the iodine oxidation product.

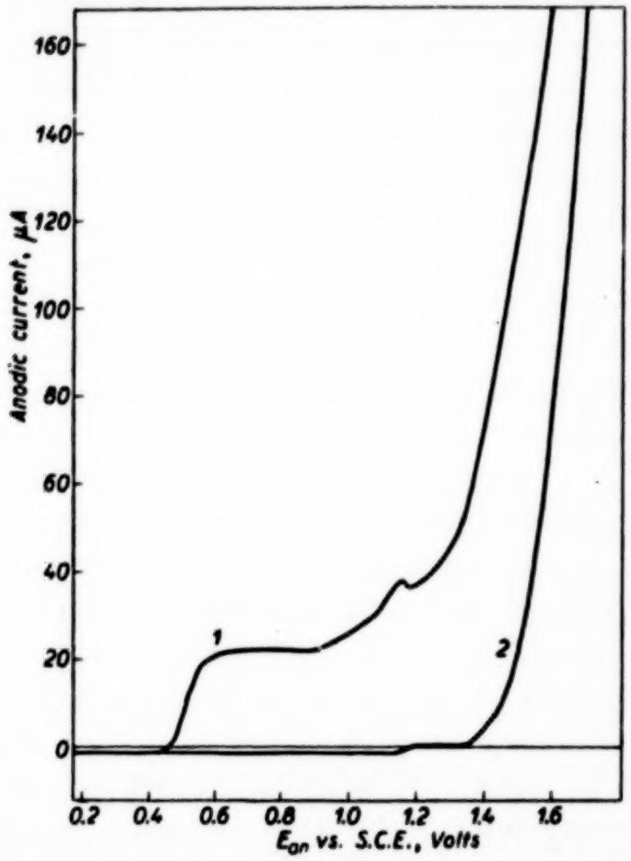

Fig. 5. Polarographically recorded anodic polarization curve of iodide ion with platinum microelectrode in stirred solution.
1. 0.3 millimolar iodide ion in 1 *F* sulfuric acid.
2. 1 *F* sulfuric acid alone.

Curve 1 in Fig. 5 is the anodic polarization curve of iodide ion in 1 *F* sulfuric acid, recorded by a polarograph with a micro platinum anode in a stirred solution. Curve 2 is the polarization curve of the acid solution alone. The well developed wave starting at +0.4 V *vs.* S.C.E. results from oxidation of iodide ion to iodine. A second limiting current is not observed, but the fact that the final current increase in curve 1 occurs distinctly in advance of the oxidation of water shows that the iodine primarily produced does indeed undergo further oxidation.

The peculiar hump at 1.1 V is reproducible when the polarization curve is recorded in the direction of increasing positive potential. If, however, the curve is recorded in the reverse direction, starting at a potential corresponding to the final current increase and decreasing the anode potential, this hump disappears. The potential at which the current begins to increase above the iodine limiting current corresponds to the standard potential (+0.953 V *vs.* S.C.E.) of the IO_3^- - I_2 couple. However, this is also close to the potential of the PtO - Pt couple. It is possible, therefore, that the peculiar characteristics of this wave, and its sensitivity to the direction of polarization, may result from the formation of a film of platinous oxide on the electrode surface which increases the overpotential for the oxidation of iodine to iodate ion.

Several investigators and most recently KOLTHOFF AND TANAKA[10], have presented evidence suggesting the formation of platinous oxide films on anodically polarized platinum electrodes.

By chronopotentiometric measurements (whose principles are discussed excellently by DELAHAY[11]) we established that iodate ion, rather than hypoiodous acid, is the oxidation product of iodine in dilute sulfuric and perchloric acid media. The chronopotentiometric measurements were performed by anodically polarizing a platinum electrode with constant current and recording the potential of the electrode as a function of time in a quiet solution. Such chronopotentiograms of iodide ion in either sulfuric or perchloric acid media show two inflections. When the iodide ion concentration is small enough so that the solubility of iodine (0.0013 *M*) is not exceeded, the ratio of the two transition times is 35. This is the value expected for successive 1- and 5-electron reactions.

That the chronopotentiogram should show an inflection for oxidation of iodine to iodate ion, although a definite iodate limiting current is not apparent on the polarographic anodic polarization curve, supports the idea that a film of platinous oxide forms on the platinum anode, provided the film forms relatively slowly. During the relatively slow recording of a polarogram there is sufficient time for an inhibiting film to form. A chronopotentiogram is recorded so rapidly that the film does not become sufficiently formed to be inhibiting. We are systematically studying the chronopotentiometry of iodide ion, and will present a complete account later.

The potential at which iodine is oxidized to iodate ion is nearly coincident with the potential at which cerous ion is oxidized. With the relatively small concentration of cerous sulfate (0.025 *F*) used for the titrations of Table I oxidation of iodine occurs at a slightly lower potential than oxidation of cerous ion, so there is considerable transient formation of iodate ion. With a large concentration of cerous sulfate (*e.g.*, 0.1 *F*) oxidation of cerous ion occurs at a lower potential and there will be less formation of iodate. However, with a large concentration of cerous sulfate the current efficiency is greatly improved, so that even though little or no oxidation of iodine occurs the net titration error will remain small.

The situation extant in the coulometric titration of iodide ion is unusual, although not unique. Relatively good titration efficiency under conditions of poor efficiency for ceric ion generation can be expected in other cases where the substance being titrated is capable of transient electro-oxidation to an oxidation state higher than the state corresponding to the titration end-point.

In the more usual circumstance, where the substance being titrated is incapable of oxidation above the state to which the titration is carried, poor efficiency for ceric ion generation leads to an almost correspondingly poor titration efficiency. The titration of ferrous iron to the ferric state is an example. In five titrations of 17.5 mg quantities of ferrous ion in 100 ml of 0.025 *F* cerous sulfate in 0.9 *F* sulfuric acid, positive titration errors ranging from 1 to 1.5% were observed (average +1.2%) when the titration was performed with a generating current density of 18 mA/cm². At this current density the generation of ceric ion is only 98% efficient, so if there had been no direct electro-oxidation of ferrous ion a positive titration error of 2% would have resulted. Comparison with the average observed error (+1.2%) indicates that about forty percent of the ferrous ion underwent direct electro-oxidation.

ACKNOWLEDGEMENT

Appreciation is expressed to the National Heart Institute for a fellowship held by one of us F(.C.A.), and to the Mallinckrodt Chemical Works for partial financial support.

SUMMARY

The current efficiency for the electrogeneration of ceric ion at a platinum anode falls considerably below 100% at both very small and at large current densities in both sulfuric and perchloric acid media. The maximal current efficiency is about 99.8%.

Iodide ion can be titrated to iodine with an error of only about ± 0.3%, even under conditions where the ceric ion generation efficiency is only 98%. High titration efficiency, in spite of poor efficiency for ceric ion generation, is obtained because iodine is oxidized to iodate ion at a potential slightly in advance of the potential at which cerous ion is oxidized. Since the electrogenerated iodate ion oxidizes iodide ion only a minor fraction of the total quantity of electricity results from ceric ion generation, so the effect of its inefficient generation is greatly minimized. Satisfactory titrations of iodide ion to iodine can be performed without any cerous salt present, provided the generating current density is smaller than the limiting current density for oxidation of iodine to iodate ion.

RÉSUMÉ

Le rendement du courant, lors de la formation de l'ion cérique à l'anode de platine baisse considérablement au-dessous de 100% soit pour des très faibles, soit pour des fortes densités de courant, en milieu sulfurique ou en milieu perchlorique. Le rendement maximum est d'environ 99.8%. L'ion iodhydrique peut être titré par oxydation en iode avec une erreur d'environ ± 0.3% seulement, même dans les conditions où le rendement de l'ion cérique n'est que de 98%. Les rendements des titrages effectués sont bons, malgré le mauvais rendement pour la formation de l'ion Ce^{+4}, l'iode étant oxydé en ion iodique à un potentiel légèrement inférieur au potentiel d'oxydation de l'ion Ce^{+3}. L'ion iodique formé oxydant l'ion iodhydrique, seulement une faible partie de la quantité d'électricité totale est due à la formation d'ions Ce^{+4} de telle sorte que l'effet du faible rendement de leur formation est grandement diminué. Des titrages de l'ion iodhydrique par oxydation en iode peuvent être effectués en l'absence de tout sel céreux, à condition que la densité de courant soit plus petite que la densité de courant limite correspondant à l'oxydation de l'iode en iodate.

ZUSAMMENFASSUNG

Die Stromausbeute für die elektrische Bildung des Ce^{+4}-Ions an einer Platinanode sinkt bei sehr geringen und bei grossen Stromdichten in Schwefelsäure sowohl als in Perchlorsäure bedeutend unter 100%. Die maximale Stromausbeute beträgt ungefähr 99.8%.

Das Jodidion kann mit einem Fehler von nur ungefähr ± 0.3% zu Jod titriert werden und zwar auch unter Bedingungen wo die Bildungsausbeute für das Ce^{+4}-Ion nur 98% beträgt. Trotz der niedrigen Ausbeute für die Bildung des Ce^{+4}-Ions erhält man eine hohe Titrationsausbeute, weil die Oxydation des Jods zum Jodation bei einem etwas früher erreichten Potential stattfindet als die Oxydation des Ce^{+3}-Ions. Da das elektrisch gebildete Jodation das Jodidion oxydiert, stammt nur ein kleiner Teil der gesammten Elektrizitätsmenge von der Bildung des Ce^{+4}-Ions wodurch die Auswirkung von dessen wenig effizienter Bildung stark verringert wird. Befriedigende Titrationen von Jodidion zu Jod können in Abwesenheit von Ce^{+3}-Ionen ausgeführt werden, unter der Bedingung dass die Stromdichte unter dem Grenzwerte für die Oxydation von Jod zum Jodation bleibt.

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A HYDROGEN-NITROGEN GAS COULOMETER

by

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The hydrogen-oxygen gas coulometer is the simplest and most convenient instrument to use for the integration of varying small direct currents, as in coulometric analysis[1]. The studies of LEHFELDT[2] and LINGANE[1] have demonstrated the good accuracy of the instrument when used with currents that do not vary over too wide a range. However, we have observed that the instrument is subject to a significant negative error when the current density at the electrodes is smaller than about 20 mA/cm².

By using hydrazine sulfate as electrolyte nitrogen is evolved at the platinum anode instead of oxygen, the anode reaction being $N_2H_5^+ = N_2 + 5H^+ + 4e$, and hydrogen ion is reduced to hydrogen at the platinum cathode. Hence the net coulometer reaction is $N_2H_5^+ = N_2 + 2H_2 + H^+$, and the theoretical volume of gas evolved per coulomb is the same as for the hydrogen-oxygen coulometer.

The hydrogen-nitrogen coulometer does not show the negative error of the hydrogen-oxygen coulometer at small currents. This indicates that the negative error of the latter is associated with the evolution of oxygen, and it probably is caused by a little formation of hydrogen peroxide at the anode concomitantly with the evolution of oxygen. Any of the hydrogen peroxide that escapes further oxidation to oxygen, and gets transferred into the solution, will undergo reduction to water at the cathode, so not only is the current efficiency for oxygen evolution decreased below 100% but that for hydrogen evolution is also decreased. The absence of this error at relatively large currents probably results from the fact that at the larger current densities the working potential of the anode becomes so positive (oxidizing) that any hydrogen peroxide transiently produced is rapidly oxidized to oxygen before it can escape into the solution.

APPARATUS AND TECHNIQUE

The instrument used in this investigation was the same as that described by LINGANE[1], but was equipped with two pairs of platinum electrodes. One pair consisted of two sheets of platinum foil, each 1 cm square, the second pair consisted of two pieces of No. 18 platinum wire, each 1 cm long. The electrodes were mounted so that the members of each pair were diametrically opposite and parallel.

The electrolytes were prepared from reagent grade salts, the hydrazine sulphate being, in addition, recrystallized from water. The volume of elctrolyte required to fill the coulometer was 125 ml, and the electrolyte was discarded and replaced after the passage of about 300 coulombs of electricity. The measuring buret, capacity 50 ml, was calibrated before use *(complete drainage)*. Before each calibration run, the electrolyte was saturated with the gases by a preliminary electrolysis employing a current of the same magnitude as that to be used in the calibration. At the end of the preliminary electrolysis, the current was stopped and, after waiting a minute or two until all the gas bubbles had risen to the surface of the electrolyte, the measuring buret was adjusted and read.

For calibration, a constant current from a regulated high voltage power supply and series resistance was passed through the coulometer. The magnitude of the current was determined by measuring with a potentiometer the potential drop across a standard resistance in series with the coulometer. In all cases the current was found to remain constant within ± 0.05%. Time was measured with an electric stop watch.

During the electrolysis, the measuring buret was continually adjusted so that the gases were collected at a pressure near to atmospheric. At the end of the electrolysis, after waiting until all the gas bubbles had risen to the surface of the electrolyte, the measuring buret was finally adjusted and read. After correction for the partial pressure of water vapor over the confining electrolyte, the volume of gas evolved was corrected to standard temperature and pressure. Additional manipulative details are available in Reference 1.

RESULTS AND DISCUSSION

Hydrogen-oxygen gas coulometer

The typical calibration data plotted in Fig. 1 show that the hydrogen-oxygen gas coulometer employing a 0.50*M* potassium sulphate electrolyte produces less lthan the theoretical volume of gas. The negative error becomes large at smal currents. The theoretical volume of the 2:1 hydrogen-oxygen gas mixture, calculated from the densities of hydrogen and oxygen, 0.08988 and 1.4290_4 g/l at S.T.P.[3], 96,493 absolute coulombs per faraday, and allowing for the volume of water decomposed in the electrolysis, is 0.1741_5 ml of gas at S.T.P. per coulomb.

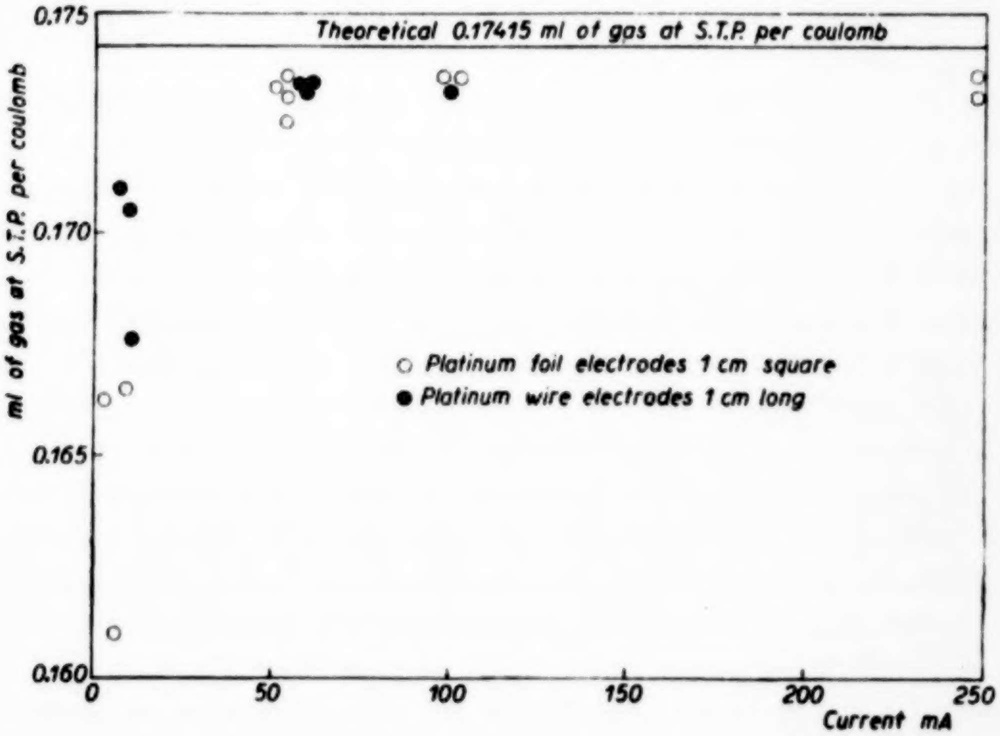

Fig. 1. Accuracy of the hydrogen-oxygen gas coulometer at various constant currents.

With currents between 50 and 250 mA, the instrument operates satisfactorily, with a slightly low but constant factor. An average value of 0.1732 ±0.0003 ml of gas at S.T.P. per coulomb, was obtained for the 12 calibration runs. With currents

References p. 179

less than 50 mA, the instrument produces significantly low results, the magnitude of the error increasing rapidly with decreasing current. The use of the small electrode pair, to maintain a larger current *density*, decreases but does not eliminate the error.

Such behavior introduces an error in a controlled potential coulometric analysis — with its continuously decreasing current — for which a correction cannot readily be made.

Hydrogen-nitrogen coulometer

The instrument was the same as the hydrogen-oxygen coulometer, except that 0.1*M* $N_2H_4 \cdot H_2SO_4$ was used as electrolyte. The capacity of this electrolyte in respect to oxidation of hydrazine to nitrogen is 4,820 coulombs for the 125 ml volume used. In the calibration experiments the electrolyte was replenished after about each 300 coulombs, although it probably would cause no harm to use the electrolyte until it is about half exhausted.

The aqueous vapor pressure of 0.1*M* hydrazine sulfate at various temperatures, which is required in correcting the observed gas volume to standard conditions, is as follows:

$t°C$	20	22	24	26	28	30
P_{H_2O}, *mm*	17.5	19.7	22.3	25.1	28.2	31.7

The data in Table I demonstrate that the hydrogen-nitrogen coulometer yields a calibration factor within about 0.3% of the theoretical value, and the factor does not change with current density as does the calibration factor of a hydrogen-oxygen coulometer. The fact that the calibration factor averages 0.3% lower than the theoretical suggests a small systematic error in measuring the gas volume in terms of the volume of electrolyte displaced into the levelling buret. A calibration factor in closer agreement with theory probably would be observed if a more orthodox gas measuring technique were used, but this would be far less convenient than the simple technique used to obtain these data.

TABLE I

ACCURACY OF THE HYDROGEN-NITROGEN GAS COULOMETER WITH VARYING CURRENTS

Theoretical volume of the 2:1 hydrogen-nitrogen gas mixture is 0.1742_7 ml/coulomb at standard conditions.

Current (mA)	*Time (seconds)*	*Coulombs*	ΔV *(ml at S.T.P.)*	ΔV *per coulomb (ml at S.T.P.)*
101.9	1500	152.8	26.64	0.1743
101.9	1500	152.8	26.67	0.1744
78.21	2107	164.8	28.47	0.1728
78.23	1616	126.4	21.93	0.1735
31.30	4681	146.5	25.38	0.1732
31.27	6237	195.0	34.01	0.1744
28.97	3900	113.0	19.68	0.1742
15.66	5920	92.71	16.11	0.1738
15.65	7030	110.0	19.17	0.1742
7.822	10000	78.22	13.54	0.1731

Average 0.1738 ± 0.0005

Micro gas coulometer

In the integration of small quantities of electricity, of the order of 5 to 20 coulombs, it was found that the gas coulometer in its usual form gave results of poor precision. The volume of the gas produced is small, and since the volume is measured by the displacement of a relatively large volume of electrolyte, small changes in either the temperature of the electrolyte or the dimensions of the flexible tubing connecting the measuring buret and the electrolysis cell can produce relatively large changes in the reading.

The new gas coulometer for the measurement of small quantities of electricity is shown in Fig. 2. The hydrogen-nitrogen gas mixture produced by the electrolysis is collected in a 5 ml buret under a short mobile column or slug of electrolyte held by capillarity in the narrow buret. The electrolysis compartment has a volume of about 25 ml, and it is connected by a length of rubber tubing to a levelling bulb. The electrodes are two pieces of platinum wire, each piece 1 cm in length. It is essential that the inside surfaces of the apparatus be smooth, to avoid trapping gas beneath the surface of the electrolyte.

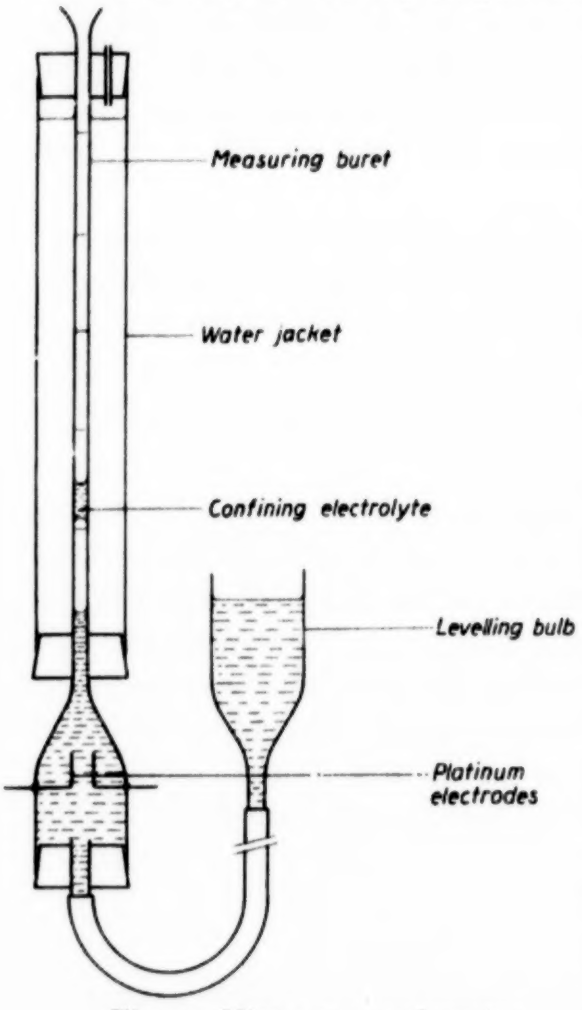

Fig. 2. Micro gas coulometer.

To prepare the coulometer for use, the apparatus is rinsed and filled with electrolyte. The electrolyte is then saturated with gas by a preliminary electrolysis. After saturation, the electrolyte level is adjusted until it is about 1 cm below the funnel top of the buret, and about 0.2 ml of water is added to the buret top. The added water traps a small volume of gas in the buret, and the electrolyte level is now adjusted to be near the bottom of the buret graduations. After waiting a few minutes for drainage, the top meniscus of the electrolyte and the lower meniscus of the water seal are read on the buret. The difference in the two readings is the initial volume of gas in the buret.

The coulometer is now ready for operation. At the conclusion of the electrolysis, and after allowing a few minutes for drainage, the top meniscus of the electrolyte and the lower meniscus of the water seal are again read. The difference of the two readings is the final volume of gas in the buret. The volume of gas produced is the difference between the initial and final volumes. In the correction to standard temperature and pressure, it is to be remembered that the gas trapped in the buret is present at a pressure slightly greater than atmospheric pressure, the difference being calculable from the length of the water seal.

The maximum value of the current that the instrument can integrate is about 20 mA. With currents above this value, the rapid evolution of gas will carry short columns of electrolyte up the measuring buret.

The performance data in Table II show that the new coulometer is an accurate

TABLE II

ACCURACY OF THE MICRO GAS COULOMETER WITH VARIOUS ELECTROLYTES

Electrolyte	*Current (mA)*	*Time (seconds)*	*Coulombs*	*ΔV (ml at S.T.P.)*	*ΔV per coulomb (ml at S.T.P.)*
0.10M $N_2H_4 \cdot H_2SO_4$	20.378	1004	20.46	3.559	0.1740
	20.378	1002	20.42	3.553	0.1740
	10.189	2052	20.91	3.645	0.1743
	10.189	2040	20.79	3.621	0.1741
	10.189	1245	12.69	2.206	0.1739
	1.0189	18520	18.86	3.285	0.1742
	1.0189	14910	15.19	2.636	0.1736
				Average	0.1740
0.50M Na_2SO_4	10.189	2078	21.17	3.638	0.1718
	10.189	2100	21.40	3.683	0.1721
0.25M $K_2Cr_2O_7$	10.189	1883	19.19	3.297	0.1718
	10.189	2048	20.87	3.598	0.1721
0.10M $HClO_4$	10.189	2085	21.24	3.649	0.1718
	10.189	2071	21.10	3.650	0.1730

instrument for integrating small currents. An average of 0.1740 ± 0.0002 ml of gas per coulomb at S.T.P. was obtained for the seven calibration experiments. Comparison runs with sodium sulphate, potassium dichromate and perchloric acid electrolytes show that the hydrogen-oxygen system gives the same low results with the new instrument as observed on a macro scale.

ACKNOWLEDGEMENT

Grateful acknowledgement is made to the National Research Council of Canada for Grant G-472 which helped to defray the expenses of this investigation.

SUMMARY

The hydrogen-oxygen gas coulometer yields a negative error at small current densities. A hydrogen-nitrogen gas coulometer, employing a hydrazine sulphate electrolyte, and free from this error, is described. A new form of the gas coulometer, employing the hydrazine sulphate electrolyte and suitable for the accurate integration of small quantities of electricity (5 to 20 coulombs) has been developed.

RÉSUMÉ

Avec le coulomètre à gaz hydrogène-oxygène on obtient une erreur négative pour les faibles densités de courant. Un coulomètre à gaz hydrogène-azote est décrit; on utilise alors comme électrolyte du sulfate d'hydrazine et l'erreur négative ne se produit plus. Un nouveau modèle de coulomètre à gaz est décrit, utilisant le sulfate d'hydrazine comme électrolyte et convenant pour une intégration précise de petites quantités d'électricité (5 à 20 coulombs).

ZUSAMMENFASSUNG

Das Wasserstoff-Sauerstoff-Gascoulometer gibt für kleine Stromdichten einen negativen Fehler. Ein Wasserstoff-Stickstoff-Gascoulometer wird beschrieben, das Hydrazinsulfat als Elektrolyt enthält und das diesen Fehler nicht ergibt. Ein neues Gascoulometer-Modell, welches den Hydrazinsulfat-Elektrolyt enthält und zur genauen Integration kleiner Elektrizitätsmengen (5 bis 20 Coulomb) geeignet ist, wurde entwickelt.

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AN AMPEROMETRIC METHOD FOR MAGNESIUM*

by

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Complexes of Pontachrome Violet SW (C.I. 169) with certain metal ions have been described[1]. These give polarographic waves whose height depends on the concentration of the complex. In this paper conditions are described which favor magnesium complex formation in preference to complexes of other cations and render the determination of magnesium in the presence of limited amounts of these cations possible.

APPARATUS AND REAGENTS

Materials

Purification of the dye has been described[1].

Eastman, technical grade, piperidine and ethylenediamine were used without purification.

The standard solution of magnesium was prepared from chemically pure basic magnesium carbonate.

Apparatus

All current-voltage curves and amperometric titration curves were made with a Sargent-Heyrovsky model XII polarograph. The titration vessel was a 50 ml beaker equipped with a stopper to support the dropping mercury capillary, a nitrogen inlet tube, and a 10 ml microburet.

All pH measurements were made with a Beckman model G pH meter equipped with the special lithium glass electrode for the pH range 7 to 14.

EXPERIMENTAL

Masking agent

A masking agent which would preferentially complex interfering cations and thus prevent the formation of their Violet SW complexes would be ideal. The stability constants of four azo dyes very closely related to Violet SW in structure have been determined[2]. The pK values are about 7 for the magnesium complexes and about 5 for the calcium complexes. Thus, any masking agent must complex magnesium ions less than this value in order not to remove magnesium from the Violet SW complex. Using tables of stability constants compiled by MARTELL AND CALVIN[3] as a guide, oxalate, citrate, tartrate, ethylenediamine and ethylenediaminetetraacetic acid were explored.

Piperidine-hydrochloric acid solutions, adjusted to pH 11.0, were used as buffers.

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Sufficient dye and masking agent was added to give a final concentration of $0.003M$ and $0.02M$, respectively. The polarogram was recorded, then a small amount of metal ion was added. A second polarogram was taken to ascertain whether a second wave appeared. If none appeared, more of the test cation was added until its range of interference was established.

Neither oxalate, tartrate, nor citrate were of value. Ethylenediaminetetraacetic acid prevented the formation of the magnesium complex. Only ethylenediamine prevented the formation of any other metal complex and yet allowed the magnesium complex to form.

Effect of pH on the magnesium-Violet SW complex

High pH favors formation of the magnesium complex but it also favors formation of the interfering calcium complex, which begins to form at pH 10.5. A series of amperometric titrations of Violet SW solutions with standard magnesium solutions were carried out in order to determine optimum pH conditions. The current was measured at a voltage which corresponded to the plateau between the wave of the dye alone and magnesium-dye complex. In each titration a 10 ml portion of the dye solution was transferred to the polarographic cell and increments of the magnesium solution were added.

At pH 9.5, and using an ammonium chloride-ammonia buffer, poor titration curves were obtained. At pH 10 better titration curves were obtained but it was noticed that the volume of standard magnesium solution consumed was dependent upon the concentration of the dye. A larger amount of magnesium was consumed for the more dilute solutions of dye. This indicates an equilibrium between the dye and magnesium ions. At pH 10.5 the volume of magnesium required still depends slightly on the concentration of the dye in the original solution. Good curves were obtained at pH 11.0 and the volume of magnesium solution required did not depend on the concentration of the dye. At higher pH values calcium interference becomes important.

The effect of diverse ions

Solutions of Violet SW were prepared as described under the standardization section. Solutions of the metal ions were added, one at a time, in small, measured quantities. Nitrogen was passed through the solution for 1 minute after each addition and before a current reading was taken. The maximum permissible concentration of each interfering ion was calculated as that concentration which causes a change of 1 per cent of the total current. Since the permitted concentration is proportional to the concentration of the magnesium solution being determined, the results in Table I are given as a fraction of that magnesium concentration.

The ions studied may be grouped into four categories:

(1) Ions which do not interfere. These include sodium, lithium, potassium, ammonium, strontium, cadmium, barium, arsenate, nitrate, bromide, phosphate, fluoride and iodide.

(2) Ions which ordinarily form a complex with the dye but which are masked by ethylenediamine. These include nickel, zinc, iron(II) and cobalt(II) in concentrations not exceeding that of magnesium.

(3) Ions which precipitate at pH 11 adsorb some of the dye. These include thorium, iron(III), chromium(III), aluminum, tin(II) and lead(II).

(4) Ions which are reduced at —0.60 volt *vs* S.C.E., or less, and thus cannot be tolerated. These are mercury(II), silver, iron(III), copper(II) and chromate.

The effect of ethylenediamine concentration on various interfering cations was

TABLE I

MAXIMUM CONCENTRATION OF INTERFERING IONS IN AMPEROMETRIC MAGNESIUM DETERMINATIONS

Ion tested	*Concentration allowed*[a]
Aluminum	0.01
Arsenic(V)	2
Barium	5
Bromide	10
Cadmium	20
Calcium	2
Chromate	0.02
Chromium(III)	0.01
Cobalt(II)	1
Copper(II)	0.01
Fluoride	10
Iodide	10
Iron(II)	1
Iron(III)	0.01
Lead(II)	0.02
Manganese(II)	0.2
Mercury	0.01
Nickel	1
Nitrate	20
Phosphate	10
Silver	0.05
Strontium	20
Tin(II)	0.01
Zinc	0.5

[a] Expressed as a factor to be multiplied by the magnesium concentration to obtain actual concentration.

TABLE II

THE EFFECT OF ETHYLENEDIAMINE CONCENTRATION OF INTERFERING METAL IONS

Each solution contained Violet SW equivalent to 5.97 millimoles of magnesium

Cation tested	*Ethylenediamine added, M*	*Equivalents of dye found, millimoles*
Nickel, 1.43 m*M*	0.36	6.10
Nickel, 1.43 m*M*	0.36	6.13
Nickel, 1.43 m*M*	0.90	5.95
Calcium, 5.0 m*M*	0.36	6.29
Calcium, 5.0 m*M*	0.90	6.27
Zinc, 1.5 m*M*	0.36	7.08
Zinc, 1.5 m*M*	0.90	6.13
Cobalt, 5.0 m*M*	0.90	6.10
Manganese, 5.0 m*M*	0.36	8.04
Manganese, 5.0 m*M*	0.90	7.76
none	none	6.08[a]
none	1.2	5.97[a]

[a] Average of three titrations.

studied by titrating a fixed amount of Violet SW with a standard solution of magnesium containing the interfering ion. The dye solutions at pH 11.0 contained varying amounts of ethylenediamine. The results in Table II show that manganese and calcium are not appreciably removed as interferences, whereas nickel, cobalt and zinc are largely eliminated.

Standardization of Pontachrome Violet SW solution

Prepare an adequate quantity of Pontachrome Violet SW solution, containing approximately 0.5 g per liter of the commercial dye. Pipette 10 ml of the dye solution into a 50 ml beaker, add 1.5 ml of piperidine, 2 ml of ethylenediamine, and adjust to pH 11.0 by adding 6*M* hydrochloric acid dropwise. Rinse the electrodes with distilled water and dilute the solution to 20 ml. Deaerate the solution with nitrogen and then run a polarogram to ascertain the correct potential for the titration (−0.60 volt *vs* S.C.E.). Select a galvanometer sensitivity which will yield a maximum reading on its scale.

Add measured quantities of the standard magnesium solution, about 0.003*M*, from a microburet. Bubble with nitrogen for 30 seconds after each addition, then allow 30 seconds for quiescent conditions to be reestablished before recording the current observed. Repeat these steps until no further change in current is observed. In the titration the decrease in wave height of the dye itself is what is being measured, rather than the increase in diffusion current due to the formation of magnesium complex, which occurs at a more negative voltage.

TABLE III

AMPEROMETRIC MAGNESIUM TITRATION IN THE ABSENCE OF OTHER METAL IONS

Each solution titrated was 0.6*M* in piperidine, 1.2*M* in ethylenediamine, and contained 10 ml of standard Violet SW solution

Magnesium, mM	*Volume required, ml*		*Magnesium consumed by dye, millimoles*
1.68	3.67		6.16
1.68	3.56		5.98
1.68	3.60		6.05
2.52	2.32		5.84
2.52	2.38		5.99
2.52	2.35		5.92
5.04	1.19		6.00
5.04	1.17		5.90
5.04	1.18		5.95
5.04	1.19		6.00
		Average	5.97 ± 0.06

Known amounts of a standard magnesium solution were used to titrate 10 ml of the standard dye solution, using the procedure described. The results are given in Table III. The volume of magnesium solution required is slightly more than expected for dilute solutions, evidently because of the instability of the complex. However, the average deviation is only 1 per cent for all concentrations. 10 ml of standard dye was equivalent to 5.97 millimoles of magnesium.

Method of processing samples

For limestone samples weigh a sample containing 0.02 to 0.20 g of magnesium, treat with a minimum of 12*M* hydrochloric acid, and separate any fine white residue by filtration through a fine-porosity, sintered-glass crucible. Wash the residue with 1*M* hydrochloric acid and discard. Transfer the solution and washings to a 1 liter volumetric flask and dilute to the mark with distilled water. Use this solution to titrate an accurately measured quantity of the dye as described in the standardization section. It is desirable to use the same amount of dye for the standardization titrations as for the unknown.

For other mineral samples, proceed with the ordinary scheme of analysis, and use the filtrate from the R_2O_3 precipitate, or an aliquot portion, for the titration. If R_2O_3 is mostly iron oxide, and constitutes less than 10 per cent of the sample, it is not necessary to remove these oxides. Amounts of iron, copper, manganese, chromium, tin, lead or aluminum in excess of those indicated in Table I for a given concentration of magnesium must be removed prior to the titration.

DISCUSSION

A buffer adjusted to pH 11.0 was chosen in order to minimize interference from calcium. Formation of the calcium complex begins about pH 10.5 and its stability increases with an increase in pH. A pH of 11 is the lowest value which will enable a good magnesium titration curve to be obtained. Consequently pH adjustment must be made to within 0.1 pH unit and adequate buffering capacity is necessary to prevent any change in pH during the titration.

It is realized that titration with the unknown solution is unorthodox. It is necessary, unfortunately, since magnesium hydroxide is precipitated at pH 11 in the absence of the dye. The alternate method of adding a known excess of dye to a test solution and back-titrating with a standard solution of magnesium was found to be inferior in accuracy.

Large amounts of inert ions cause no interference, a distinct advantage over Eriochrome Black T[4,5] methods. In practice, more iron(III) and copper(II) can be tolerated than indicated by Table I. These ions cause a constant increase in diffusion current for each increment of titrant, which alters the slopes of the two branches of the titration curve, but without shifting the point of intersection.

Magnesium solutions as dilute as $3 \cdot 10^{-4} M$ can be used. However, the optimum range of concentrations is 0.001 to $0.01 M$. Within this range an accuracy of 1 per cent is easily attained. The results of the determination of rather large amounts of magnesium in Bureau of Standards (U.S.A.) samples are given in Table IV.

TABLE IV

MAGNESIUM DETERMINATIONS OF BUREAU OF STANDARDS SAMPLES

Bureau of Standards sample	*Major components, %*		*MgO found, %*
Dolomite 88	Fe_2O_3	0.084	21.9
	Al_2O_3	0.067	22.1
	CaO	30.49	21.7
	MgO	21.48	21.9
	Nonmetallic	47.39	22.3
			avg. 22.0 ± 0.2
Burned Magnesite 104	Fe_2O_3	7.07	85.5
	Al_2O_3	0.84	86.7
	CaO	3.35	85.5
	MgO	85.67	86.1
			84.9
			avg. 85.7 ± 0.5

SUMMARY

An amperometric method for the estimation of magnesium has been devised based on the polarographic wave given by the magnesium complex with Pontachrome Violet SW. Titrations are carried out at a pH of 11 in the presence of ethylenediamine to prevent interference from small amounts of other cations. An accuracy of 1 per cent is obtained under ideal conditions. No preliminary separations are necessary for most types of limestones.

RÉSUMÉ

Une méthode ampérométrique a été établie pour le dosage du magnésium; elle est basée sur la vague polarographique obtenue avec le complexe magnésium-violet pontachrome SW. Les titrages sont effectués au pH 11, en présence d'éthylènediamine pour empêcher de petites quantités d'autres cations de gêner. Une exactitude de 1% est obtenue dans les conditions idéales. Aucune séparation préliminaire n'est nécessaire pour l'analyse de la plupart des types de calcaire.

ZUSAMMENFASSUNG

Eine amperometrische Bestimmungsmethode wird beschrieben, die sich auf die polarographische Welle des Magnesium-Pontachromviolett SW-Komplexes gründet. Die Titrationen werden bei pH 11 in Gegenwart von Äthylendiamin ausgeführt um Störungen durch kleine Mengen anderer Kationen auszuschalten. Unter idealen Bedingungen kann eine Genauigkeit von 1% erzielt werden. Für die Analyse der meisten Kalksteinarten sind vorherige Trennungen nicht erforderlich.

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AMPEROMETRIC TITRATION OF CERIUM(III) WITH FERRICYANIDE

by

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INTRODUCTION

Cerous cerium is most often determined reductimetrically after complete oxidation to the ceric state. When ceric salts are already present in the sample, a determination by difference is necessitated, which becomes increasingly uncertain as the ratio of tetravalent to trivalent cerium in the samples becomes larger. Among the various direct methods for the determination of cerous salts which had been proposed at the time this investigation was undertaken, that of Tomiček[1] appeared to be the most reliable. We were able to verify his findings that ferricyanide titration of cerous salts dissolved in concentrated potassium carbonate gives accurate and precise results when the end-point is determined potentiometrically. The method is much less attractive when the ratio of ceric to cerous ions in the sample is large, however, as then the titration curve starts out rising steeply, and precise determination of the end-point becomes very difficult. In order to avoid this drawback, we have investigated the possibility of determining the end-point amperometrically and have found this technique to give very satisfactory results. An amperometric titration of cerium with permanganate was reported by Goffart[2] while this investigation was being carried out.

EXPERIMENTAL

Apparatus and materials

Exploratory polarograms were obtained by means of a Sargent Model XXI recording polarograph. Titrations were performed with a simple manual polarograph incorporating a lamp and scale galvanometer for direct reading of the current (the Fisher Elecdropode). Inasmuch as experience showed the most favorable potential for carrying out the titration to be O.O.V. *versus* the S.C.E., the only equipment that is actually necessary is a sensitive microammeter. The titration cell was a 100 ml beaker, the stopper of which had holes for the buret tip (a 5.000 ml microburet), the flexible salt bridge leading to the large saturated calomel working electrode[3], a nitrogen bubbler, and the rotating platinum electrode.

The latter was of the simple platinum-sealed-in-glass type described by Laitinen and Kolthoff[4] and was rotated at about 800 r.p.m. by a small induction motor. It was found convenient to have a glass-enclosed iron stirring bar in the cell and mix the solution with a magnetic stirrer after each addition of reagent.

Distilled water and reagent-grade chemicals were used throughout. The stock cerous nitrate solutions were $0.02M$ in trivalent cerium and $0.4M$ in nitric acid. Potentiometric titration with air-free ferricyanide solution under the conditions recommended by Tomiček, and persulfate oxidation followed by ferrous sulfate titration to a 1-10 phenanthroline end-point gave good agreement in the standardization of these solutions.

Experimental

Exploratory polarograms with the rotating platinum electrode were run to determine the feasibility and probable optimum conditions for an amperometric titration with ferricyanide. Figure 1 shows three current-voltage curves representing the residual current of the air-free $3.6M$ potassium carbonate solution, a mixture $0.5\ mM$ each in cerous and ceric ions in $3.6M$ potassium carbonate, and a similar mixture of ferrocyanide and ferricyanide ions. It is evident that the residual current of the carbonate supporting electrolyte is negligible and that the electro-oxidation and reduction of cerium is quite irreversible under these conditions. It can be seen that the most favorable conditions for an amperometric titration should be found between about +0.3 V, the oxidation potential of the ferrocyanide-ferricyanide couple, and about —0.4 V where the ceric carbonate complex begins to be reduced. Amperometric titrations were performed at several potentials and it was concluded that the optimal conditions were obtained at 0.0 V *versus* the S.C.E. There the convenience of working without the necessity of special apparatus for applying potential is combined with a very favorable difference in the change of diffusion currents before and after the equivalence point. In actual practice, the indicator electrode current is very close to zero at the equivalence point. A typical titration curve is shown in Figure 2.

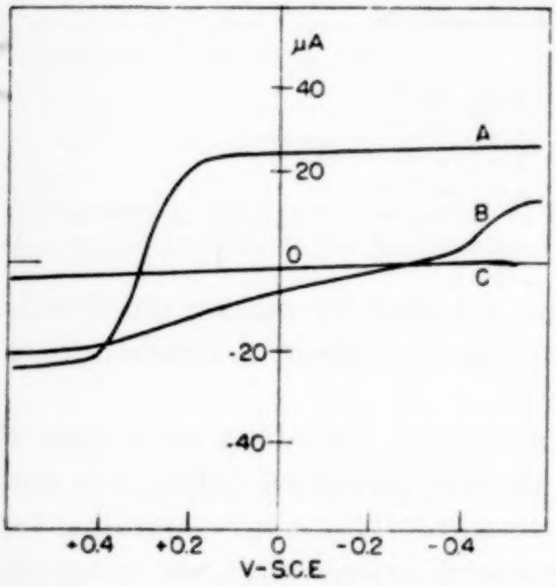

Fig. 1. Automatically recorded current-voltage curves at the rotating platinum microelectrode.

A. $0.5 \cdot 10^{-3} M$ $[Fe(CN)_6]^{-3}$ and $0.5 \cdot 10^{-3} M$ $[Fe(CN)_6]^{-4}$ in $3.6 M$ K_2CO_3.
B. $0.5 \cdot 10^{-3} M$ Ce(III) and $0.5 \cdot 10^{-3} M$ Ce(IV) in $3.6 M$ K_2CO_3.
C. Residual current of $3.6 M$ K_2CO_3.

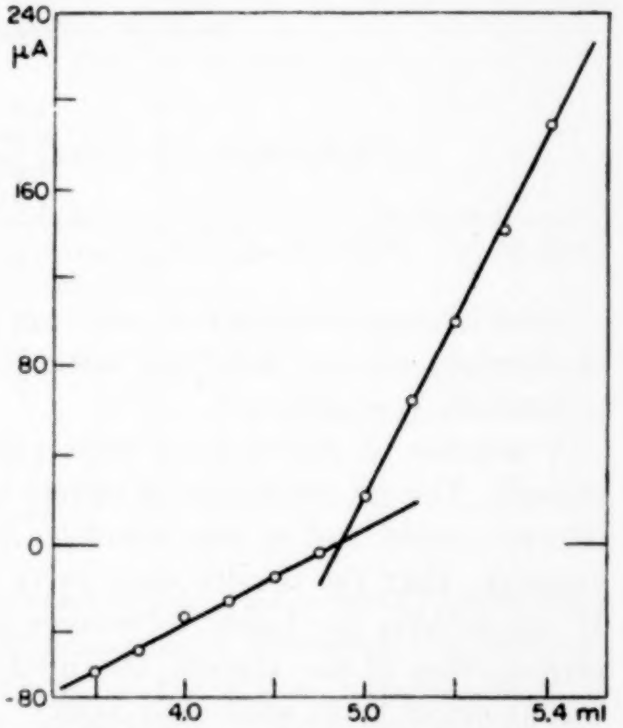

Fig. 2. Amperometric titration of a 6.86 mg of Ce in 50 ml of $3.6 M$ potassium carbonate with approximately $0.01 M$ potassium ferricyanide. Theoretical end-point at 4.97 ml.

Procedure

To the cell is added 50 ml of stock $3.6 M$ potassium carbonate solution. Nitrogen is bubbled through the solution for 10-15 minutes and then the sample solution (1-10 ml) is added while the nitrogen flow continues. The sample itself should also be purged with water-washed nitrogen beforehand if the most exact results are required. The gas inlet is raised above the surface and a brisk stream of nitrogen continued. The salt bridge is introduced, the rotation of the electrode begun and the titration performed with standard air-free potassium ferricyanide of a concentration appropriate to the sample being determined. For 1-6 mg of trivalent cerium, titration with $0.01 M$ ferricyanide in a 5.00 ml microburet is suitable.

Results

The above procedure was found to give satisfactory results in the 1-10 mg range using stock cerous nitrate solutions as samples. A series of ten 6-mg samples run by one analyst gave a precision (standard deviation) of 0.6% and the error of the average value was —0.4%. A second analyst in a series of eight samples found a standard deviation of 0.9% and an error of —0.5%. As was expected, the presence of considerable amounts of ceric ion had no disturbing influence. When 6-mg quantities of cerous ion were determined in the presence of a 100-fold excess of ceric ion in ceric ammonium nitrate, excellent results were obtained for the cerous added if the ceric solution were pre-titrated with ferricyanide to remove cerous impurity prior to addition of the cerous sample. In a series of six such titrations, a standard deviation of 0.6% and an error in the mean value of only +0.2% was found. Table I shows some of the typical results obtained during this study.

TABLE I

TITRATION OF CE(III) IN THE PRESENCE OF CE(IV)

Ce(IV), M	*Ce(III) added, M*	*Ce(III) found, M*
0.4	$4.95 \cdot 10^{-3}$	$4.93 \cdot 10^{-3}$
0.1	$1.96 \cdot 10^{-3}$	$1.94 \cdot 10^{-3}$
0.1	$1.96 \cdot 10^{-4}$	$2.0 \cdot 10^{-4}$
0.1	$4.95 \cdot 10^{-5}$	$4.3 \cdot 10^{-5}$

Greater concentrations of ceric ion could not be obtained by mixing stock ceric ammonium nitrate solutions with potassium carbonate without formation of a permanent precipitate.

A number of experiments were performed to determine the effect of oxygen if present. The air oxidation of cerous ions in the alkaline carbonate solution is moderately rapid and it was found in the titration of $2 \cdot 10^{-3} M$ cerous solutions, for example, that the results were 15 to 20 per cent low if oxygen were not removed. If precautions are taken to remove oxygen from the carbonate solution prior to introduction of the sample, the method is well adapted to the determination of cerous impurity in solid ceric salts.

ACKNOWLEDGEMENT

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SUMMARY

Milligram and larger quantities of cerous cerium may be determined accurately and precisely, even in the presence of large amounts of ceric salts, by amperometric titration in 3 to $4M$ potassium carbonate solution with potassium ferricyanide. A rotating platinum microelectrode held at the potential of the saturated calomel electrode is recommended.

RÉSUMÉ

Des quantités de cérium(III) de l'ordre du milligramme et des quantités supérieures peuvent être dosées par ampérométrie avec exactitude et précision, même en présence de grandes quantités de cérium(IV); le titrage s'effectue dans une solution de carbonate de potassium 3 à $4M$ au moyen du ferricyanure de potassium. Une micro-électrode tournante en platine, maintenue au potentiel de l'électrode au calomel saturée, est recommandée.

ZUSAMMENFASSUNG

Cer(III) kann in Mengen von der Ordnung des Milligramms oder in grösseren Mengen, auch in Gegenwart von grossen Mengen an Cer(IV)-Salzen durch amperometrische Titration mit Kaliumferricyanid in 3 bis $4M$ Kaliumcarbonatlösung genau bestimmt werden. Eine drehende Platin-Mikroelektrode, deren Potential auf der Höhe des Potentials der gesättigten Calomelelektrode gehalten wird, wird empfohlen.

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REPRODUCIBILITY OF RADIOACTIVE SAMPLE PREPARATION TECHNIQUES

by

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INTRODUCTION

The successful application of radionuclides for tracing purposes is usually dependent upon a convenient and reproducible technique of measurement. In essence, the measurement of radioactivity consists in placing a sample of the active material near a suitable detector and determining the effect of the emissions from the sample on the detector. The agreement of results from a series of such measurements made under identical conditions is an indication of the reproducibility of sample preparation techniques.

One of the most widely used techniques of sample preparation involves the evaporation of a known amount of radioactive solution on the surface of a small planchet. Various methods for obtaining good reproducibility have been described[1,2,3]. HUME[4] has pointed out the importance of the sample preparation by stating that the physical form of the sample has more effect upon the reproducibility than the combined effect of statistical fluctuations in the radioactivity, coincidence losses in the detector, and changes in the efficiency of the detector.

Various estimates of the error involved in the preparation of evaporated samples have been made. KOHMAN[3] stated that the best routine techniques gave reproducibility only to the extent of 1 to 3 per cent. CALVIN[5] pointed out that the mean deviation from the mean was about 4 per cent for samples of carbon-11 (emitting a 0.99-Mev positron) pipeted onto a thin piece of blotting paper and then dried. With carbon-14 (a 0.16-Mev beta-emitter) solutions evaporated onto glass or aluminum mounts, the mean deviation was reported to be about 3.0 to 5.0 per cent in the 0.0 to 1.0 mg/cm^2 range, 1.5 to 4.0 per cent in the 1.0 to 4.0 mg/cm^2 range, and 1.5 to 2.5 per cent in the 4.0 to 10 mg/cm^2 range. COOK AND DUNCAN[6] have said that, with reasonable care, results obtained with evaporated samples on cupped aluminum planchets about 1/8 inch deep were accurate within 5 per cent. SELIGER AND SCHWEBEL[7] reported that the individual standard deviation was usually less than 0.3 per cent when solutions of phosphorus-32 (a 1.70-Mev beta-emitter) were evaporated on flat discs.

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In the present investigation, the authors have studied in more detail than has been reported previously the reproducibility of radioactive sample preparation by direct evaporation of a solution of a radionuclide on a planchet.

EXPERIMENTAL

All radioactive nuclides were obtained from the Oak Ridge National Laboratory. Sulfur-35, a 0.17-Mev beta-emitter, was used for the low-energy beta experiments. Phosphorus-32, a 1.70-Mev beta-emitter, was used for the high-energy beta experiments. The 0.66-Mev gamma ray emitted by cesium-barium-137 was used in the gamma experiments. All nuclides were carrier free.

Beta-emitting samples were counted with a mica-window Geiger tube of 2.5 mg/cm^2 surface density. Impulses from the tube were recorded on a scale-of-256 scaling unit. Gamma-emitting samples were counted with a scintillation spectrometer. The detector consisted of a 1 inch by 1 1/2 inch diameter thallium-activated sodium iodide crystal and a photomultiplier tube. The impulses from the photomultiplier tube were passed through a single-channel scintillation spectrometer[8] and recorded on a scale-of-512 scaling unit. Beta particles were not detected in the scintillation counter at the pulse height setting required for counting the gamma rays from cesium-barium-137. This was tested by means of a gamma-ray spectrum determination on a sample of the gamma-emitting nuclide. The sample to detector distance in both systems was approximately 0.8 cm.

Samples for all determinations were prepared by rinsing the pipet with the radioactive solution, transferring a 100-lambda aliquot to the sample mount, and then rinsing the pipet with 100-lambda of water, which was added to the mount. The same pipet was used for all samples in a given series consisting of thirty sample mounts. All sample mounts were 1 inch in diameter, except the aluminum ones, which were 1 1/4 inches. All mounts were flat discs with the exception of the steel ones, which were cups 1/4 inch high. Sample mounts for each experiment were carefully cleaned immediately before use. The solution of the nuclide was deposited on the center of the mount with no restriction on the amount of spreading. After deposition, the solutions on the sample mounts were dried under a 250-watt infrared lamp. The samples were placed on a thick paper board at a distance of about 23 cm from the lamp. Five mounts were dried at a time, all five being equally spaced on the circumference of a circle of about 10 cm diameter.

STATISTICAL TREATMENT

A very useful quantity in making estimates of error is the nine tenths or reliable error E. The probability of making an error greater than this value is 0.10. For a sample population of thirty, the reliable error of a single observation will be 1.7 times the standard deviation[9]. The per cent reliable error $\%E$ will be given by:

$$\%E = \frac{100\ E}{A} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (1)$$

where A is the average for the series of thirty samples.

The actual disintegration rate of a radioactive sample continuously fluctuates because of the random nature of the disintegration process. The per cent reliable error of a given radioactivity determination may be expressed by[10]:

$$\%E = 1.65\ \frac{(S/t_s^2 + B/t_b^2)^{1/2}}{(S/t_s - B/t_b)} \times 100 \quad \ldots\ldots\ldots\ldots \quad (2)$$

where S is the total number of counts recorded in time t_s with the sample in place, and B is the background count or the number of counts recorded in time t_b with the sample removed. A sufficient number of counts were observed in each determination to keep the per cent reliable error due to the random disintegration process less than 0.5 per cent. This figure therefore serves as a limit below which no definite conclusions can be drawn.

RESULTS

A total of five experiments were performed. In the first experiment, the variable chosen was the molarity of sodium chloride in solution with the carrier-free nuclide. All solutions at a pH value of 7.0 and were deposited on copper planchets. Results from this experiment are given in Table I. The variable chosen in the second experiment was the type of mount. All solutions contained 0.01*M* sodium chloride at a pH value of 7.0. These results are given in Table II. The third experiment had the pH value of the solution as a variable. All solutions contained 0.01*M* sodium chloride and were deposited on copper planchets. Results from this experiment are given in Table III. In the fourth experiment, the effect of auxiliary mounting media was studied.

TABLE I

PER CENT RELIABLE ERROR OF RADIOACTIVE SAMPLES PREPARED WITH VARIABLE TOTAL SOLIDS

Molarity of NaCl[a]	*% E for samples of*		
	P-32	*S-35*	*Cs-137*
0.00	1.7	2.2	2.4
0.01	1.6	2.9	1.6
0.10	2.1	4.1	1.0
1.00	3.0	20.9	1.1
5.00	6.4	22.4	2.2

[a] All solutions at pH 7 and deposited on copper planchets.

TABLE II

PER CENT RELIABLE ERROR OF RADIOACTIVE SAMPLES PREPARED ON VARIOUS TYPES OF MOUNTS

Sample mount material[a]	*% E for samples of*		
	P-32	*S-35*	*Cs-137*
Copper	1.6	2.9	1.6
Glass	2.5	7.9	3.3
Aluminum	1.7	2.8	4.2
Steel cups	5.1	3.4	1.1

[a] All solutions contained 0.01*M* NaCl at pH 7.

TABLE III

PER CENT RELIABLE ERROR OF RADIOACTIVE SAMPLES PREPARED FROM SOLUTIONS OF VARIABLE PH VALUES

pH[a]	*% E for samples of*		
	P-32	*S-35*	*Cs-137*
2.0	1.4	2.1	1.3
4.0	1.2	2.8	1.4
7.0	1.6	2.9	1.6
10.0	0.9	2.6	1.4

[a] All solutions contained 0.01*M* NaCl and were deposited on copper planchets.

TABLE IV

PER CENT RELIABLE ERROR OF RADIOACTIVE SAMPLES PREPARED ON AUXILIARY POROUS MOUNTING MEDIA

Auxiliary media[a]	*% E for samples of*		
	P-32	*S-35*	*Cs-137*
None	5.1	3.4	1.1
Lens paper	1.6	6.9	3.5
Filter paper	1.4	11.2	2.2

[a] All solutions contained 0.01*M* NaCl at pH 7 with the auxiliary media contained in steel cups.

TABLE V

PER CENT RELIABLE ERROR OF RADIOACTIVE SAMPLES PREPARED FROM SOLUTIONS CONTAINING A WETTING AGENT[a]

% E for samples of		
P-32	*S-35*	*Cs-137*
4.2	5.2	2.9

[a] All solutions contained 0.01*M* NaCl and 1 per cent sodium lauryl sulfate at pH 7. Copper planchets were used.

References p. 193

Solutions of the nuclides containing 0.01*M* sodium chloride at a pH value of 7.0 were used, and nickel-plated steel cups held the auxiliary media. Filter paper discs 0.03 inch thick were cut to fit the bottom of the cups. Solutions were deposited on these discs and dried. Lens paper discs were stuck to the bottom of the cups with 300-lambda of a 5 per cent sucrose solution (which gave an added surface density of about 3 mg/cm^2) to prevent buckling. The solution of the radionuclide was then deposited and dried. Results from this experiment are given in Table IV. In the final experiment, the effect of a wetting agent was studied. Solutions of the three nuclides containing 0.01*M* sodium chloride and 1 per cent sodium lauryl sulfate (DuPont U.S.P. grade) were prepared at a pH value of 7.0. Samples were made by deposition on copper mounts and subsequent evaporation. The results of this experiment are given in Table V.

For most samples, the size of the active deposit was about 1 cm diameter as shown by autoradiograms of the surface of the planchet. The active deposits produced in the wetting agent experiment were extremely variable and covered most of the surface area of the planchet. Autoradiograms of samples from the first three experiments showed similar deposition patterns. The active deposit formed a narrow ring about 1 cm diameter at the periphery of the drop with faint amounts of activity within the ring. The bulk of the active deposit in the wetting agent experiment concentrated in the central portion of the drop with smaller amounts extending out to the periphery of the drop. Autoradiograms were not attempted of the deposits made in the cupped planchets.

The variables chosen in this investigation were judged to be the most common ones encountered in samples prepared by evaporation of a liquid.

CONCLUSIONS

The results of this investigation showed that the amount of total solids present in solution of a beta-emitting nuclide is an important factor affecting the reproducibility of samples prepared from such a solution. The influence of solids upon reproducibility is greater for low-energy beta-emitters than for higher energy ones. The use of a single-channel scintillation spectrometer for counting gamma radiations gave better reproducibility for sample preparation at high total solid concentrations than did the use of a beta-detector for counting beta-particles.

From the four types of sample mounts studied, it was found that copper and aluminum planchets gave the most reproducible results for the two beta-emitters, and that copper planchets and steel cups gave better results for the gamma-emitter.

Hydrogen ion concentration had little effect on sample preparation for solutions of all three nuclides.

The use of auxiliary porous media and the presence of a wetting agent in solution did not enhance the reproducibility of samples prepared from the nuclides studied.

SUMMARY

The reproducibility of samples prepared for the determination of radioactivity has been investigated for a low-energy beta-emitting nuclide, a high-energy beta-emitting nuclide, and a gamma-emitting nuclide.

Variables studied, in addition to the nature of the nuclide, were: the total solid concentration in solution, the nature of the sample mount, the pH value of the solution, the use of auxiliary porous media (paper), and the effect of a wetting agent.

High total solid concentration had a great effect on the reproducibility of measurements made with the low energy beta-emitter, and a less pronouced effect on measurements made with the high energy beta-emitter. The effect of total solids was negligible for measurements of the gamma-emitter using a single-channel scintillation spectrometer.

Copper or aluminum planchets gave best reproducibility for the beta-emitting nuclides, whereas copper planchets or steel cups were best for the gamma-emitter.

The effect of the other factors studied was negligible under conditions of this investigation.

RÉSUMÉ

L'influence de quelques facteurs sur la réproductibilité d'échantillons préparés pour la mesure de la radioactivité a été étudiée, d'une part pour des émetteurs de rayons β d'énergie faible et d'énergie élevée, d'autre part pour un émetteur de rayons γ.

Les différents facteurs étudiés sont: la concentration totale des sels étrangers (NaCl), la nature du support, le pH de la solution, l'emploi de supports poreux auxiliaires (papier), et l'effet d'un agent mouillant.

Les concentrations élevées de sels étrangers ont une grande influence sur la réproductibilité des mesures d'échantillons d'émetteurs β de faible énergie, mais peu prononcée pour les émetteurs β d'énergie élevée. L'influence est négligeable pour les émetteurs de rayons γ mesurés au scintillateur.

Les supports en forme de disques de cuivre ou d'aluminium donnent les meilleurs résultats avec les émetteurs β, les supports en forme de coupes de cuivre ou d'acier sont à préférer pour les émetteurs γ.

L'influence des autres facteurs étudiés est négligeable dans les conditions employées.

ZUSAMMENFASSUNG

Die Reproduzierbarkeit der Herstellung von Proben für Radioaktivitätsbestimmungen ist im Falle weicher Beta-Strahler, harter Beta-Strahler, und Gamma-Strahler untersucht worden.

Unter den studierten Variablen befanden sich ausser der Natur des Isotops die Gesamtkonzentration fester Körper in Lösung, der Typ des Probenhalters, der pH-Wert der Lösung, der Gebrauch poröser Materialien (Papier), und der Einfluss eines Netzmittels.

Eine hohe Gesamtkonzentration fester Körper hatte einen grossen Einfluss auf die Reproduzierbarkeit der mit einem weichen Beta-Strahler gemachten Messungen, und einen nicht so ausgeprägten Einfluss auf die mit einem harten Beta-Strahler gemachten Messungen. Der Einfluss der Gesamtkonzentration fester Körper war nicht wichtig für Messungen des Gamma-Strahlers mit einem Einkanalscintillationszähler.

Kupfer- oder Aluminiumscheiben lieferten mit den Beta-Strahlern die beste Reproduzierbarkeit, während mit den Gamma-Strahlern Kupferscheiben oder flache Stahlschälchen am besten funktionierten.

Unter den Untersuchungsbedingungen war der Einfluss anderer Faktoren vernachlässigbar.

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THE POLAROGRAPHIC DETERMINATION OF ALUMINIUM IN ZINC-BASE DIE-CASTING ALLOYS

by

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Zinc-base die-casting alloys have about 4% of aluminium, a low or modest percentage of copper, and very low percentages of magnesium, iron, lead, cadmium, and tin (Table I). The impact strength of these alloys is adversely affected if the concentration of aluminium is greater than 4.5%; if it reaches 5%, the alloy is extremely brittle. To avoid the danger of impairment of strength by excessive aluminium, the upper limit for this element in the specifications for the commonest types of die-casting alloy (those in which the concentration of copper is not greater than 1.25%) is 4.3% for both ingots and castings. The lower limit should be sufficiently high to avoid loss of castability and other undesirable effects associated with an unduly low content of aluminium, sufficiently far removed from the maximum value for aluminium to allow reasonable latitude in making the alloys, and yet sufficiently close to the maximum to ensure careful alloying practice. The American specification for the lower limit in ingots is 3.9%, and, in castings, 3.5%; the corresponding figures in the British specifications are 3.9% and 3.8%.

No method for the polarographic determination of aluminium in zinc-base die-casting alloys appears to have been published, although polarographic methods have been developed for the determination in these alloys (and in zinc metal) of several other elements. A review of the problems associated with the direct polarographic determination of aluminium, and the considerations that led us to adopt a supporting electrolyte of magnesium chloride ($0.150 M$) and sodium sulfate ($0.045 M$) of fixed pH, are given in another paper[1].

The present paper describes, and gives the results of, the application to die-casting alloys of our method for the direct polarographic determination of aluminium. Interfering ions are removed from a solution of the alloy by a prior electrolysis in a mercury-cathode cell, and the interference of the hydrogen discharge, which just precedes that of aluminium, is nullified by careful control of pH before polarographing. Analyses of standard samples of die-casting alloys from three different laboratories by this method yielded results that are of good precision and that agree with those of umpire-grade analyses by gravimetric (oxide and 8-hydroxyquinolate) and spectrographic methods.

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TABLE I

SPECIFICATIONS FOR ZINC-BASE ALLOY DIE CASTINGS* (%)

Element	*A.S.T.M. Alloy AG40A*	*British Alloy A*	*A.S.T.M. Alloy AC41A*	*British Alloy B*	*A.S.T.M. Alloy AC43A*
Aluminium	3.5-4.3	3.8-4.3	3.5-4.3	3.8.-4.3	3.5-4.5
Copper	0.15 (max.)	0.10 (max.)	0.75-1.25	0.75-1.25	2.5-3.5
Magnesium	0.03-0.08	0.03-0.06	0.03-0.08	0.03-0.06	0.02-0.10
Iron	0.100(max.)	0.10 (max.)	0.100(max.)	0.10 (max.)	0.100(max.)
Lead	0.007(max.)	0.005(max.)	0.007(max.)	0.005(max.)	0.007(max.)
Cadmium	0.005(max.)	0.005(max.)	0.005(max.)	0.005(max.)	0.005(max.)
Tin	0.005(max.)	0.002(max.)	0.005(max.)	0.002(max.)	0.005(max.)
Zinc	Remainder	Remainder	Remainder	Remainder	Remainder

* American Society for Testing Materials (A.S.T.M.) Specification B86-53T for Alloys AG40A, AC41A, and AC43A. British Standards Institution Specification 1004:1955 for Alloys A and B; this Specification also states that thallium should not exceed 0.001%, nor indium 0.0005%.

APPARATUS AND REAGENTS

Apparatus

An Heyrovský polarograph (Model XI, E. H. Sargent and Co., Chicago, U.S.A.) was used. The sensitivity of the galvanometer, redetermined for each "run" (*vide infra*), was close to 0.141 microamp/mm at the setting $R = 50$ (at which all measurements were made). The capillary was of special tubing supplied by E. H. Sargent and Co. (#S-29350). The pressure of mercury for the capillary was regulated and controlled ($h = 47.0$ cm) by a Castaloy Levelling Bulb Support (Fisher Scientific Co., Montreal, Canada). When polarographic waves showed irregularities traceable to fluctuations in drop time, the capillary was cleaned with nitric acid as directed by KOLTHOFF AND LINGANE[2]. The value of $m^{2/3}t^{1/6}$ at 25.0°C in an air-free medium 0.15*M* in magnesium chloride and 0.045*M* in sodium sulfate, containing bromophenol blue ($8 \cdot 10^{-5}$%) and at a pH of 3.66, was 1.578 mg$^{2/3}$ sec.$^{-1/2}$ at —1.59 volts, and 1.538 mg$^{2/3}$ sec.$^{-1/2}$ at —1.74 volts, both potentials *vs* the saturated calomel electrode.

All polarographic determinations were carried out in an H-type cell, using a saturated calomel reference electrode. The cell was similar to the one described by LINGANE AND LAITINEN[3]; the calomel electrode and agar plug were prepared in the way described by MEITES[4].

The pH meter was Model No. 7662 of the Leeds and Northrup Company (Philadelphia, U.S.A.) equipped with electrodes #1199-30 (glass) and #1199-19 (saturated calomel). The meter was frequently standardized by means of a 0.0500 molal solution of potassium hydrogen phthalate prepared by the method recommended by the National Bureau of Standards (Washington, U.S.A.) but using an analyzed grade of phthalate after recrystallization according to the directions of KOLTHOFF AND SANDELL[5].

Unless otherwise stated, the mercury-cathode cell was of the Melaven type, constructed from a 250-ml wide-mouthed Erlenmeyer flask, and described elsewhere[6]. Before use it was charged with 50 ml of purified mercury to give a cathodic surface area of 40 cm^2. The anode was a flat, stationary, spiral of platinum wire.

Reagents

The mercury for the dropping electrode, calomel cell, and mercury-cathode cell was purified by washing it in 20% nitric acid and then in water, and finally doubly distilling it *in vacuo*.

The standard solutions of aluminium for calibrating the polarograph were prepared by dissolving in hydrochloric acid spectrographically standardized aluminium (Johnson Matthey and Co. Ltd., London, England), the purity of which was estimated by the supplier to be 99.995%. The standard solutions of zinc required for the investigation of the efficiency of the mercury-cathode separation were prepared by dissolving 20-mesh zinc metal of analyzed grade in hydrochloric acid, followed by appropriate quantitative dilutions.

The potassium chloride for the calomel cell was a special grade of the reagent designed for this use, and the agar was Bacto-Agar (Difco Laboratories Inc., Detroit, U.S.A.). The bromophenol blue indicator solution (0.04%) was prepared according to a standard method[7].

All other reagents, apart from the gelatin used as a maximum suppressor in the experiments with zinc, were of analyzed grade quality.

REMOVAL OF INTERFERING IONS

For the direct polarographic determination of aluminium the solution should be relatively free of constituents that reduce at potentials less negative than that required for the reduction of aluminium; the discharge of aluminium occurs at such a negative value that appreciable concentrations of only a few ions (*e.g.*, those of the alkali and alkaline earth elements) can be tolerated. Zinc, and to a lesser extent copper, are the interfering elements in the polarographic determination of aluminium in zinc-base die-casting alloys, other elements normally being present in too low a concentration to interfere (Table I). Zinc and copper, and a score of other elements for that matter, can be removed from solution by electrolysis in a mercury-cathode cell, with quantitative retention of the aluminium in the electrolyte. This method of separation has been widely used for the separation of aluminium from interfering elements in different alloys[8] and is recommended by the American Society for Testing Materials[14] for the removal of zinc from die-casting alloys before the determination of aluminium as the oxide or 8-hydroxyquinolate.

We have found that all but 0.03% of the zinc can be removed from a one-gram sample of alloy in 40 min without much attention from the analyst. The residual zinc causes no difficulty in the subsequent polarographic determination of aluminium; in fact, up to about 1% of the original zinc can be tolerated.

Efficiency of zinc removal

One-gram samples of a die-casting alloy (Zamak-3) were treated with sulfuric acid and sodium hydroxide as given under "Procedure" (below), and then electrolyzed in the mercury-cathode cell as described there except that the electrolyses were carried out for varying periods of time (10-55 min). Afterwards, the electrolyte was drained and washed from the cell, and made up to 100.0 ml. From this volume, a 50.0-ml aliquot sample was taken, 10.7 g of ammonium chloride and 16.5 ml of $15M$ NH_3 and 5.0 ml of 0.02% gelatin dispersion were added, and the solution diluted to 100.0 ml. A portion of this solution, after removing oxygen from it by bubbling with purified nitrogen, was polarographed over the range —1.0 to —2.0 volts, *vs* a saturated calomel reference electrode. The wave for zinc was recorded, using an appropriate galvanometer sensitivity, and its height translated into terms of residual zinc by reference to a straight-line calibration curve obtained by measurements on waves given by standard solutions of zinc in the ammonia-ammonium chloride electrolyte. This supporting electrolyte has been recommended by LINGANE[9], and we have found it very satisfactory indeed.

The rate of removal of zinc from the solution is shown in Fig. 1. After 40 min of electrolysis, the removal was 99.97% complete; this was little improved by a further 15 min of electrolysis.

Similar experiments were carried out with five-gram samples of alloy, using a Melaven-type cell constructed from a 250-ml beaker with the bottom shaped to facilitate draining, and containing about 30 ml of purified mercury. Electrolysis at a cathodic current density of 0.28 amp/cm^2 for one hour removes 99.99% of the zinc ion. (In fact, in 1.5 hours zinc can be quantitatively removed from a 10-gram sample of alloy.) Some advantage is gained by using a high current density (0.50 amp/cm^2) at the beginning of the electrolysis, and then lowering it in a few minutes (before the solution comes to a boil). This is analogous to the "hot-start" method of CHIRNSIDE, DAUNCEY, AND PROFFITT[10]. Such procedures increase somewhat the rate of zinc removal in the early stages of the electrolysis. Up to a point, this rate increases with increasing cathodic current density: however, current densities higher than 0.30 amp/cm^2 cause excessive evaporation. With other conditions of electrolysis fixed, the efficiency of zinc removal decreases with increasing initial acidity of the solution.

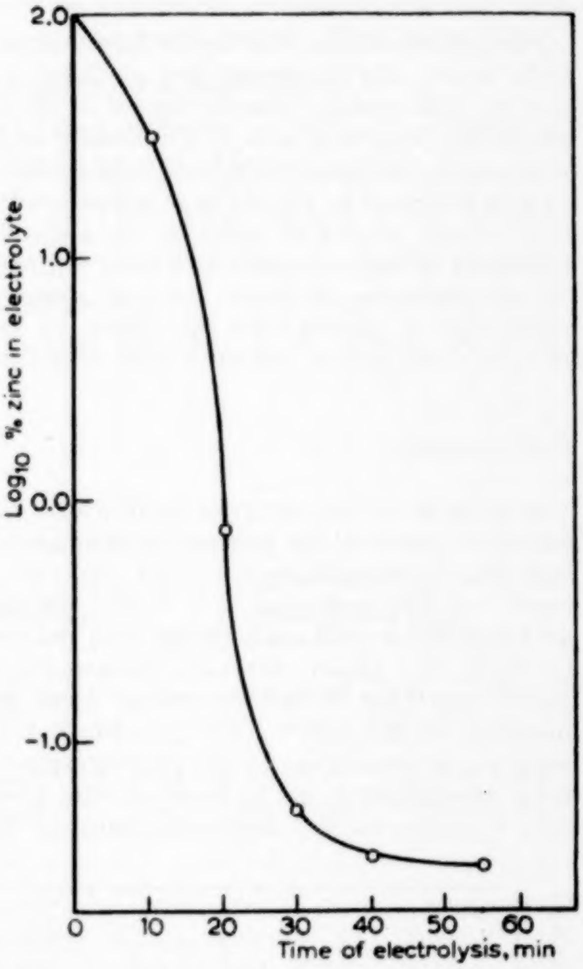

Fig. 1. Rate of removal of zinc in the mercury-cathode cell.

Other elements

Apart from zinc and aluminium, the elements copper, lead, cadmium, iron, tin, magnesium, and sometimes others occur in measureable concentration in these alloys. Magnesium, having a higher discharge potential than aluminium, offers no interference; the other elements should all be quantitatively separated from the aluminium in the mercury-cathode electrolysis[8]. We have found that the following elements (at concentrations up to at least 2% of the alloy) are sufficiently removed in the mercury-cathode procedure that they cause no interference in the polarographic determination of aluminium: cadmium, chromium, cobalt, copper, iron, lead, nickel, silver, and tin.

PROCEDURE

A solution of the alloy is electrolyzed, supporting electrolyte is added, the pH is carefully adjusted, and then the solution is polarographed. The concentration of aluminium is assessed by reference to a calibration curve obtained using standard solutions of aluminium. The detailed procedure follows:

Dissolution and electrolysis

A sample of one gram of alloy turnings is weighed accurately and then treated with 25.0 ml of 1.8*M* sulfuric acid in a 150-ml beaker. After about 20 minutes the mixture is warmed to complete the decomposition of the alloy. The solution is then cooled, the beaker is washed down with water, and a $5M$ solution of sodium hydroxide added dropwise until a small quantity of hydrous (zinc) precipitate persists. The contents of the beaker are then washed into the mercury-cathode cell and the volume adjusted with water to about 75 ml. The solution is electrolyzed for one hour, with the voltage being adjusted in the range 9-5 volts to maintain a current of 5.0 amp (cathodic current density of 0.12 amp/cm^2).

pH adjustment

After electrolysis, the electrolyte is drained into a 100-ml volumetric flask and the cell washed with water, the washings being added to the flask. The flask is then made up to volume, at 25.0°C, with water. Exactly 10 ml of the mixed solution is pipetted into another 100-ml volumetric flask, 10.0 ml of a $1.50M$ solution of magnesium chloride added by a pipet, and then 4 drops of a 0.04% solution of bromophenol blue added to serve both as a maximum suppressor and as a pH indicator. The pH of the solution is adjusted to within the range 3.62-3.68 using first a $1.0M$ and finally a $0.10M$ solution of sodium hydroxide, the adjustment being made with slow additions of the reagents and with vigorous agitation of the solution to prevent the precipitation of any hydrous alumina. (A pH meter should be used in the adjustment of the pH until experience is gained with the colour of the indicator.) The solution is then diluted to the mark at 25.0°C to give a solution that is $0.150M$ in $MgCl_2$ and $0.045M$ in Na_2SO_4.

Polarography

A portion of the solution is decanted into the polarographic cell, bubbled for 15 minutes with nitrogen (purified by passing it through a solution of chromous sulfate and then distilled water), and then polarographed at 25.0° ± 0.1°C from −1.0 to −2.0 volts *vs* the saturated calomel electrode (bridge potential, 2.0 volts; galvanometer sensitivity, $R = 50$). Each solution is polarographed twice and each of the two polarograms, which are recorded photographically on Kodabromide E-2 paper, are each measured once by the method described by WILLARD, MERRITT, AND DEAN[11] for ill-defined waves. Each photographic record is calibrated by the method recommended by MEITES[12]. This procedure takes account of any variation, from one polarogram to another, in shrinkage of the photographic paper. The sensitivity determinations varied somewhat from one polarogram to another, the average value (with maximum deviation from the average) was 0.1409 ± 0.0005 microamp/mm at $R = 50$.

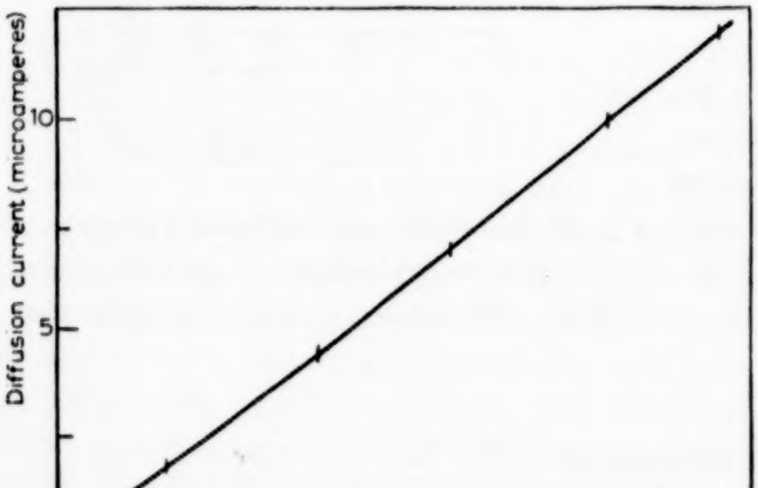

Fig. 2. Calibration curve based on measurements involving standard solutions of aluminium.

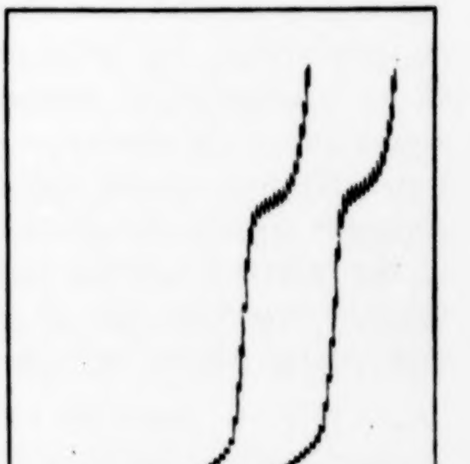

Fig. 3. Typical waves obtained with a sample of a standard alloy.

The average of the two wave heights, measured in mm, is converted to microamperes of diffusion current. The concentration of aluminium is obtained from the diffusion current by reference to a calibration curve (Fig. 2) prepared from measurements made using solutions of known aluminium content. The standard solutions of aluminium of course contain magnesium chloride ($0.150M$) and sodium sulfate ($0.045M$) at the appropriate pH and are polarographed under the same conditions as are the solutions containing aluminium at a concentration to be assessed.

References p. 200

RESULTS

The polarographic wave obtained for aluminium by this method is cleanly separated from that due to the discharge of the supporting electrolyte, but coalesces with that due to the discharge of hydrogen (Fig. 3). Reproducible recording and measurement of the wave due to a given concentration of aluminium can be made, however, providing that the pH is carefully controlled. This is essential because the extent of the wave due to hydrogen is a function of the pH of the solution. The considerations that led us to adopt a pH of 3.65 ± 0.03 are discussed elsewhere[1].

The results of the application of this polarographic method to several standard samples of zinc-base die-casting alloys are given in Table II. The standard samples were analyzed, mainly by gravimetric methods, in the laboratories from which they originated. In one or another of these alloys, the concentration of the copper was as high as 2.8%, of lead 0.03%, and of magnesium 0.11%; the concentration of the other elements were within the specification limits for A.S.T.M. Alloy AG40A or AC41A (Table I).

TABLE II

COMPARISON OF POLAROGRAPHIC AND OTHER METHODS (% Al)

Sample	*Certified values*	*Polarographic values*	
		Individual determinations	*Average*
National Bureau of Standards			
Zinc-Base Die-Casting Alloy No. 94	3.92	3.93, 3.89, 3.97	3.93 ± 0.04
Zinc-Base Die-Casting Alloy No. 94A	3.90[a]	3.97, 3.95, 3.90	3.94 ± 0.04
Apex Smelting Company			
D2080-E	4.05[b]	3.99, 4.02, 3.98	4.00 ± 0.02
D2080-C2	4.68[b]	4.74, 4.67, 4.73	4.71 ± 0.04
D2080-G	3.20[b]	3.21, 3.24, 3.20	3.22 ± 0.02
Canadian Westinghouse Company			
1940	3.99[c] 4.00[d]	3.94, 3.96, 3.88	3.93 ± 0.05

[a] Weighed as Al_2O_3, after precipitation with NH_3 or 8-hydroxyquinoline; 8 determinations; spread: 3.88-3.95%.

[b] Weighed as Al_2O_3, after precipitation by the 8-hydroxyquinoline method of the A.S.T.M.[14], slightly modified; checked spectrographically.

[c] Weighed as Al_2O_3, after precipitation by the urea-succinate method of WILLARD AND TANG[13]; 5 determinations; spread: 3.96-4.01%.

[d] 8-hydroxyquinoline method of A.S.T.M.[14]; 4 determinations; spread: 3.98-4.01%.

DISCUSSION

The reproducibility of this polarographic method is comparable to that of gravimetric procedures used for this element in this kind of alloy, and the agreement with the "certified values" is satisfactory. The method should be applicable to other substances in which the only interfering elements are among those removed by electrolysis in a mercury-cathode cell.

References p. 200

ACKNOWLEDGEMENTS

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SUMMARY

A procedure for the direct polarographic determination of aluminium is described, with particular reference to zinc-base die-casting alloys. Interfering elements are removed by electrolysis of a solution of the alloy in a mercury-cathode cell. The solution is polarographed at a carefully controlled pH in a supporting electrolyte of magnesium chloride and sodium sulfate of appropriate concentration. The precision and accuracy of the method are shown to be satisfactory by the analysis of standard samples from three different laboratories.

RÉSUMÉ

Une méthode est décrite pour le dosage polarographique direct de l'aluminium, en particulier dans les alliages de zinc pour coulée sous pression. Les éléments gênants sont éliminés par électrolyse d'une solution de l'alliage dans une cuve à cathode de mercure. La solution est polarographiée à pH soigneusement ajusté, dans une solution de base, renfermant du chlorure de magnésium et du sulfate de sodium. La précision et l'exactitude de la méthode sont satisfaisantes, elles ont été contrôlées par l'analyse d'échantillons étalons de trois laboratoires différents.

ZUSAMMENFASSUNG

Ein Verfahren zur direkten polarographischen Bestimmung von Aluminium, insbesondere in Spritzguss-Zinklegierungen wird beschrieben.

Die störenden Elemente werden aus der Lösung der Legierung durch Elektrolyse in einer Zelle mit Quecksilberkathode entfernt. Die Lösung wird bei genau eingestelltem pH in einem Magnesiumchlorid und Natriumsulfat enthaltenden Basiselektrolyt polarographiert. Die Genauigkeit der Methode ist befriedigend, was aus der Analyse von Standardproben aus drei verschiedenen Laboratorien hervorgeht.

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LES INDICATEURS ACIDES COMME RÉACTIFS SENSIBLES DES ALCALOÏDES

par

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Dans un travail antérieur sur l'emploi des "amphi-indicateurs" (combinaisons d'indicateurs acides colorés "*Δ*" avec des bases organiques "*B*") en acidimétrie biphasée[1] nous avons étudié qualitativement l'influence de quelques alcaloïdes sur la répartition de différents indicateurs dans l'eau et dans le chloroforme, en fonction du pH.

L'étude quantitative de l'influence en question a conduit ensuite à une méthode de dosage indirect de petites quantités d'alcaloïdes[2]. En effet, en amenant la phase aqueuse à un pH excluant la dissolution de toute trace du colorant dans le chloroforme on peut, dans des conditions déterminées, extraire par ce solvant des quantités d'indicateur toujours équivalentes à celles de la base contenue dans le système.

Dans ces conditions, la coloration de la phase chloroformique peut aussi servir de test pour la recherche des bases azotées.

Afin d'apprécier la sensibilité qu'offriraient différents indicateurs, nous avons effectué une série d'essais comparatifs, ayant adopté les conditions suivantes:

Facteurs constants:	Volume de la phase aqueuse, Volume de la phase chloroformique, Concentration d'indicateur, pH de la solution aqueuse, Intensité de la coloration produite.
Facteur variable:	Concentration de base azotée.

Pour chaque essai, nous partions d'une solution $1 \cdot 10^{-2} M$ d'alcaloïde. Cette solution était diluée au dixième avec le mélange tampon convenant à chaque indicateur, c'est-à-dire pH 3.6 pour le bleu de thymol (TB), pH 4 pour le bleu de bromophénol (BPB), pH 4.2 pour le pourpre de bromocrésol (BCP) et pour l'alizarine sulfonate de sodium (NAS), pH 5.4 pour le vert de bromocrésol (BCG), pH 6 pour la tropéoline OO (TOO), pH 7.5 pour le bleu de bromothymol (BTB) et pH 9 pour l'alizarine GG (AGG). A 4 ml de cette liqueur diluée portés dans un tube à essai nous ajoutions 0.05 ml de solution aqueuse d'indicateur à 0.1% et nous agitions le mélange avec 1 ml de chloroforme. Par cette première dilution, nous obtenions, dans la plupart des cas, une réaction très intense. Nous répétions alors l'essai en diluant chaque fois plus fortement la solution de l'alcaloïde par le même tampon, jusqu'à l'obtention d'une réaction très faible, mais nettement discernable. La teinte jaunâtre d'une solution alcoolique $4 \cdot 10^{-6} M$ de bleu de bromothymol, nous a servi de témoin de réaction limite.

Les résultats de nos essais sont réunis dans le tableau suivant.

TABLEAU I

Alcaloïdes	*TB*	*BPB*	*NAS*	*BCP*	*BCG*	*TOO*	*BTB*	*AGG*
Pilocarpine (PL)	$1 \cdot 10^{-3}$	$1 \cdot 10^{-4}$	—	—	$2.5 \cdot 10^{-4}$	—	$1.25 \cdot 10^{-5}$	$5 \cdot 10^{-3}$
Éphédrine (EP)	$1 \cdot 10^{-3}$	—	—	—	$3 \cdot 10^{-4}$	—	$1 \cdot 10^{-5}$	$1 \cdot 10^{-3}$
Codéine (CD)	$4 \cdot 10^{-5}$	$1 \cdot 10^{-6}$	$1 \cdot 10^{-3}$	$1.25 \cdot 10^{-5}$	$1.25 \cdot 10^{-5}$	$1 \cdot 10^{-5}$	$0.5 \cdot 10^{-5}$	$2 \cdot 10^{-3}$
Procaïne (PR)	$5 \cdot 10^{-5}$	$1 \cdot 10^{-5}$	$2.5 \cdot 10^{-4}$	$1 \cdot 10^{-5}$	$1 \cdot 10^{-5}$	$2 \cdot 10^{-5}$	$0.25 \cdot 10^{-5}$	$4 \cdot 10^{-4}$
Émétine (EM)	$0.4 \cdot 10^{-5}$	$2 \cdot 10^{-6}$	$0.5 \cdot 10^{-4}$	$0.2 \cdot 10^{-5}$	$0.4 \cdot 10^{-5}$	$0.2 \cdot 10^{-5}$	$0.5 \cdot 10^{-5}$	$2 \cdot 10^{-3}$
Spartéine (SP)	$2.5 \cdot 10^{-5}$	$5 \cdot 10^{-6}$	$2.5 \cdot 10^{-4}$	$0.25 \cdot 10^{-5}$	$0.5 \cdot 10^{-5}$	$0.5 \cdot 10^{-5}$	$0.4 \cdot 10^{-5}$	$1 \cdot 10^{-5}$
Atropine (AT)	$2 \cdot 10^{-5}$	$5 \cdot 10^{-6}$	$1 \cdot 10^{-3}$	$1 \cdot 10^{-5}$	$0.75 \cdot 10^{-5}$	$1 \cdot 10^{-5}$	$0.1 \cdot 10^{-5}$	$5 \cdot 10^{-5}$
Strychnine (ST)	$0.5 \cdot 10^{-5}$	$2 \cdot 10^{-6}$	$0.5 \cdot 10^{-4}$	$0.25 \cdot 10^{-5}$	$0.25 \cdot 10^{-5}$	$0.5 \cdot 10^{-5}$	$0.1 \cdot 10^{-5}$	$2.5 \cdot 10^{-4}$
Quinidine (QD)	$0.2 \cdot 10^{-5}$	$1 \cdot 10^{-6}$	$1.25 \cdot 10^{-5}$	$0.17 \cdot 10^{-5}$	$0.25 \cdot 10^{-5}$	$0.2 \cdot 10^{-5}$	$0.4 \cdot 10^{-5}$	$2 \cdot 10^{-5}$
Quinine (QN)	$0.2 \cdot 10^{-5}$	$0.5 \cdot 10^{-6}$	$2 \cdot 10^{-5}$	$0.17 \cdot 10^{-5}$	$0.25 \cdot 10^{-5}$	$1.3 \cdot 10^{-5}$	$0.2 \cdot 10^{-5}$	$2 \cdot 10^{-5}$

Les chiffres figurant dans ce tableau (qui, d'ailleurs peuvent être réduits considérablement par un changement opportun des volumes respectifs des deux dissolvants) indiquent les concentrations minimums nécessaires pour déceler, par cette technique, différents alcaloïdes, en employant différents indicateurs aux pH convenables. On voit donc que la sensibilité de la méthode proposée est incomparablement plus grande que celle obtenue avec les réactifs classiques de Mayer, Scheibler, Dragendorff, Godeffroy, etc., surtout dans le cas des bases hydrosolubles, dont les combinaisons avec tous les agents de précipitation mentionnés ont, en général, une solubilité considérable dans l'eau (Tableau II). La nouvelle méthode a en outre le grand avantage de permettre de déceler une base azotée directement dans des milieux troubles ou fortement colorés.

TABLEAU II

Réactif	*Strychnine*	*Quinine*	*Atropine*	*Codéine*	*Éphédrine*	*Pilocarpine*
Acide picrique	1 : 80 000		1 : 1 000	1 : 2 000	1 : 15	
Réactif de Mayer	1 : 150 000	1 : 125 000	1 : 7 000		1 : 15	1 : 6 000
Réactif de Godeffroy		1 : 50 000	1 : 15 000		1 : 500	1 : 3 600
Réactif de Scheibler	1 : 200 000	1 : 100 000				
Réactif de Dragendorff	1 : 250 000	1 : 200 000	1 : 25 000	1 : 17 500		
Bleu de bromophénol	1 : 1 500 000	1 : 6 000 000	1 : 700 000	1 : 3 500 000		1 : 50 000
Bleu de bromothymol	1 : 3 000 000	1 : 1 500 000	1 : 3 500 000	1 : 700 000	1 : 650 000	1 : 400 000

Les réactions obtenues avec différents alcaloïdes par un indicateur donné ne présentent évidemment pas la même intensité, car l'influence sur la répartition du colorant ne dépend pas seulement de la solubilité individuelle de la base recherchée, mais aussi de sa constante de dissociation et surtout des solubilités partielles des corps $B\Delta$ respectivement formés. Par exemple, l'émétine formé avec le bleu de bromothymol une combinaison très peu soluble dans l'eau, mais qui en outre se dissout difficilement dans le chloroforme. Le précipité qui résulte produit, lors de l'agitation des couches, une émulsion persistante et ce n'est que par centrifugation ou après un long repos que l'équilibre de répartition peut être atteint, avec ou sans disparition complète de la phase solide. Par contre, la procaïne, base donnant en général des réactions moins fortes que l'émétine à cause de sa plus grande solubilité dans l'eau, forme pourtant avec le bleu de bromothymol une combinaison se dissolvant beaucoup plus facilement dans le chloroforme que celle de l'émétine. Par suite cet indicateur permet de déceler la procaïne en concentration plus faible que l'émétine.

La sensibilité décroît évidemment si l'on effectue l'essai à un pH plus fort que celui caractérisant le virage "alcalin" de l'indicateur. A pH plus faibles, elle augmente quand la base est soluble dans l'eau. Avec les alcaloïdes peu solubles, l'intensité de la réaction est constante jusqu'à une certaine limite de concentration en ions hydrogène, au-dessus de laquelle celle-ci diminue. L'explication de ces faits est donnée par les courbes de solubilité déjà tracées[2]. Il est à noter toutefois qu'au-dessous des pH optimums, l'indicateur passe en partie dans le solvant organique sous forme de molécules incolores (structure lactonique des sulfone-phtaléines) et peut être ionisé par n'importe quelle substance extractible par le chloroforme, de caractère basique (selon les conceptions de Brönstedt), comme par exemple les alcools, etc. En présence de bases très solubles et en absence, bien entendu, de corps protophiles, on peut appliquer l'essai à des régions plus acides.

En résumé, chaque indicateur se comporte diversement envers différentes bases et chaque base peut offrir une réaction d'intensité variable avec différents indicateurs. Parmi les alcaloïdes choisis (abstraction faite de la quinine et de la quinidine, bases donnant des réactions très intenses avec tous les indicateurs) ceux qui produisent le maximum d'effet sur la répartition des huit indicateurs essayés sont:

pour la tropéoline OO: l'émétine,
pour l'alizarine sulfonate de sodium: l'émétine et la strychnine,
pour le bleu de bromophénol: la codéine,
pour le vert de bromocrésol: la strychnine,
pour le pourpre de bromocrésol: l'émétine,
pour le bleu de bromothymol: l'atropine et la strychnine,
pour le bleu de thymol: l'émétine et
pour l'alizarine GG: la spartéine.

Inversement, le maximum de sensibilité pour la caractérisation des alcaloïdes suivants est obtenu à l'aide des indicateurs mentionnés en regard:

spartéine: pourpre de bromocrésol,
emétine, quinine, quinidine, codéine: bleu de bromophénol,
strychnine, atropine, éphédrine, procaïne, pilocarpine: bleu de bromothymol.

Ainsi, le bleu de bromothymol et le bleu de bromophénol peuvent être considérés comme des réactifs généraux des alcaloïdes, ce qui pourrait être en partie attribué, à la plus grande puissance colorante de ces réactifs, comparée à celle des autres indicateurs envisagés.

Bibliographie p. 206

La confrontation des associations du Tableau I de notre article sur l'emploi des combinaisons $B\Delta$ en acidimétrie biphasée[1] avec celles du Tableau I du présent mémoire, montre que l'ensemble des associations "sensibles", se confond avec les amphi-indicateurs à limites de pH étroites. Les couples peu sensibles par contre correspondent aux amphi-indicateurs ayant un domaine de saut large.

Un fait plus important est la confirmation indirecte des limites "alcalines" des amphi-indicateurs figurant dans ledit tableau par les chiffres exprimant les sensibilités respectivement trouvées. Si l'on tient compte des différences qui existent entre ces deux séries d'expériences en ce qui concerne le rapport $[B]:[\Delta]$, on voit que les résultats obtenus s'harmonisent, en effet, parfaitement. La coïncidence est la plus frappante dans les cas où le rapport de concentration est identique ou ne diffère que peu. Par exemple on a observé que l'éphédrine en solution $3 \cdot 10^{-4}M$, tamponnée à pH 5.4, donne avec le vert de bromocrésol la coloration-limite. La concentration de l'indicateur dans cet essai étant $1.5 \cdot 10^{-5}$, le quotient $[B]:[\Delta]$ est donc 20. Avec ce même rapport moléculaire on a remarqué, en étudiant le domaine de pH de l'amphi-indicateur éphédrine-vert de bromocrésol, que la décoloration de la phase chloroformique a lieu à pH 5.7. Les résultats concernant les associations: pilocarpine-vert de bromocrésol et strychnine-alizarine GG, correspondant à des rapports de concentration très voisins, concordent de même parfaitement.

Malgré la diversité des voies suivies, on voit donc qu'il y a un accord parfait entre les remarques faites et les résultats atteints au cours de ces deux études, dont les buts étaient pourtant complètement différents.

Jusqu'ici nous ne nous sommes occupés que de la coloration-limite, c'est-à-dire, celle qui a servi comme témoin de comparaison dans l'étude des sensibilités. Une augmentation de la concentration du milieu en base organique entraîne évidemment que l'intensité de cette réaction colorée se trouve augmentée. Mais dans le cas où l'indicateur utilisé est un acide relativement fort et si la concentration de la phase chloroformique en base azotée vient à être plus grande que celle de l'indicateur (ce qui dépend du pH de la phase aqueuse), le chloroforme peut présenter toutes les nuances correspondant aux différents états de dissociation du colorant*.

Par exemple la strychnine en solution $2 \cdot 10^{-6}M$ donne avec le bleu de bromophénol à pH 4 la réaction-limite, c'est-à-dire une coloration jaune très pâle. A pH 4.6 on obtient (pour $[\Delta]$ identique) une coloration de même intensité avec une solution de strychnine vingt-cinq fois plus concentrée. Avec des concentrations plus fortes, on obtient au même pH des extraits chloroformiques d'une nuance grenat plus ou moins vive selon la concentration en base. Si on effectue l'essai à pH plus fort, la strychnine même en solutions très étendues, produit des colorations rosâtres. Parce que dans ce cas la condition $[B] > [\Delta]$ est toujours remplie dans la phase chloroformique, puisque par une augmentation du pH, la concentration de l'indicateur dans celle-ci diminue, tandis que celle de la base croît. Dans les mêmes conditions les alcaloïdes émétine, quinine et quinidine, ionisant plus fortement le bleu de bromophénol, communiquent au chloroforme des teintes allant jusqu'au violet.

Le vert de bromocrésol se comporte d'une façon analogue. Il se transforme en grande partie en sa forme quinonique, lorsque la concentration du colorant dans le chloroforme est inférieure de celle de la base. Il se produit une coloration violette s'il s'agit de quinine ou de quinidine et une teinte bordeaux en présence de strychnine, d'émétine et d'atropine. L'effet optique produit par la spartéine sur ces deux indicateurs est singulier. On obtient en sa présence des extraits, dont la teinte, suivant la concentration en alcaloïde, au lieu de virer du jaune au violet, passe du jaune au bleu franc en couvrant toute la gamme du vert. D'après I. M. KOLTHOFF[4] ce phénomène serait dû à l'absorption des rayons rouges par la spartéine quand elle se trouve en solutions non-aqueuses et, par conséquent, à la suppression du dichroïsme connu des colorants en question.

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* Ce comportement de certaines sulfophtaléines peut servir pour le titrage des alcaloïdes en milieu chloroformique[3].

Bibliographie p. 206

Lorsque la sulfone-phtaléine est un acide très faible, la transformation tautomérique s'arrête à la forme phénolique du colorant. Par suite, la réaction se manifeste toujours par une coloration jaune indépendamment du pH, de la solubilité, du pK et de la concentration de l'alcaloïde.

Il existe, par conséquent, une relation intéressante entre le pH, le rapport $[B]:[\Delta]$ et la teinte des deux liquides qui pourrait servir à l'identification des alcaloïdes. Par exemple, les dix bases dont nous nous sommes spécialement occupés peuvent être aisément identifiées par 3 ou 4 essais selon le schéma indiqué dans le Tableau III.

TABLEAU III

Réactif	*pH*	*Nuance de la phase aqueuse*	*Nuance de la phase chloroformique*	*Base probablement présente*	*Base certainement présente*
BCG	6	Bleu intense	Incolore		EP
			Jaune pâle	PL	
		Bleu pâle	Jaune vif	CD, PR, AT	
			Brique	EM	
		Incolore	Jaune	ST, SP	
			Bordeaux	QD	
			Violet	QN	
BPB	4	Lilas	Jaune très pâle		PL
BPB	5·5	Violet	Incolore		CD
			Jaune vif		PR
BCG	6.5	Bleu	Jaune		AT
		Bleu ciel	Chair		EM
BPB	6.5	Violet	Incolore		ST
			Bleu de Prusse		SP
BPB	7·5	Rose pâle	Rose intense		QD
		Violet vif	Violet pâle		QN

Mode opératoire

Procéder d'abord par titrage direct[2], à l'aide d'une solution $5\cdot10^{-3}M$ de bleu de bromothymol, à la détermination de la concentration moléculaire approximative de l'échantillon en alcaloïde. Diluer ensuite le liquide de sorte à obtenir une solution environ $1\cdot10^{-3}M$. Pour chaque essai, prélever 2 ml de cette solution, ajouter 0.1 ml d'indicateur en solution aqeuse $1\cdot10^{-3}M$, 3 ml de tampon et 5 ml de chloroforme. Le quotient des concentrations finales comporte ainsi le rapport $\frac{[B]}{[\Delta]} = \frac{4\cdot10^{-4}}{2\cdot10^{-5}} = 20$ et tous les effets optiques sont bien conformes à ceux illustrés au Tableau I de notre étude sur les amphi-indicateurs[1].

Bibliographie p. 206

Le Tableau III n'offre évidemment qu'un exemple de la marche systématique possible. A remarquer, en outre, que les chiffres du Tableau I peuvent aussi servir avantageusement pour la confirmation des résultats. Il suffit de noter par exemple que l'éphédrine donne avec l'alizarine GG à pH 9 une réaction cinq fois plus forte que la pilocarpine: que la procaïne avec le même indicateur et au même pH, produit une coloration cinq fois plus accentuée que la codéine et 12 fois plus intense que la pilocarpine; que la sensibilité du bleu de thymol envers l'émétine est dix fois plus grande qu'avec la codéine, etc.

Les possibilités offertes sont donc si nombreuses qu'il est permis de prévoir qu'une application sur une échelle plus vaste, du principe que nous venons de décrire brièvement, ne présenterait pas de difficultés insurmontables.

Un toxicologue ou un analyste travaillant sur un nombre restreint de bases végétales, pourrait sans doute compléter cette étude selon le principe décrit en utilisant éventuellement d'autres indicateurs, d'autres solvants aprotoniques, etc.

RÉSUMÉ

Les auteurs décrivent une méthode sensible, permettant la recherche et, sous certaines conditions, l'identification des bases azotées, reposant sur la propriété de ces dernières de former avec différents indicateurs acides des combinaisons colorées, facilement extractibles par le chloroforme.

SUMMARY

A sensitive method for the detection of organic bases is described. It is based on the property of the latter to react with several indicator acids yielding coloured compounds, readily extractable by chloroform. The circumstances under which this method could lead to the identification of alkaloids are also investigated.

ZUSAMMENFASSUNG

Es wurde eine empfindliche Methode für den Nachweis organischer Basen ausgearbeitet, die unter bestimmten Voraussetzungen auch für die Identifikation von Alkaloiden dienen könnte. Das Prinzip der Methode beruht auf der Eigenschaft obiger Basen mit Indikatorsäuren in gefärbte Additionsverbindungen überzugehen die in Wasser schwer, in Chloroform dagegen leicht löslich sind.

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TITRATION OF BASIC GROUPS IN ION-EXCHANGE RESINS WITH PERCHLORIC ACID IN GLACIAL ACETIC ACID

by

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The increasing interest in chelating resins[1] as distinct from the conventional ion-exchange type has led to the preparation of numerous resins containing a variety of different functional groups. In this synthetic field the determination of the extent to which a given reaction for the introduction of a particular functional group has proceeded is not always evident from ultimate analyses and a determination of the functional groupings present provides a much superior method of characterizing any given resin.

The determination of basic groups in organic compounds by titration with standardized perchloric-acetic acid mixtures with visual indicators is well established[2]. One of the advantages gained by working with this system is that the basicity of a group in glacial acetic acid is considerably enhanced over its value in water, so that many groups which cannot be titrated against aqueous hydrochloric acid titrate satisfactorily with perchloric acid in glacial acetic acid.

We have recently synthesized a number of resins containing amino and other basic groupings and have examined their behaviour towards perchloric acid in glacial acetic acid. The majority of the resins were based on the cross linked polystyrene matrix and were therefore insoluble in acetic acid. Reaction at room temperature with perchloric acid was found to be excessively slow for convenience but at 90-100° reaction was fairly rapid at least until the vicinity of the end-point. Not only did the increased temperature enhance the rate of diffusion of the reagent into the resin but also, in many cases it appeared to promote swelling and disintegration of the resin.

Two methods were examined. The first consisted of direct titration with perchloric acid using Crystal Violet or Oracet Blue B as indicator; the second involved reaction with excess perchloric acid and back titration with a standardized solution of sodium acetate in glacial acetic acid with the same indicator.

Reagents

Perchloric acid, 0.1N in glacial acetic acid. No free acetic anhydride should be present. B.D.H. commercially available material is suitable. Standardize periodically against potassium hydrogen phthalate.

Sodium acetate, 0.1N in glacial acetic acid. Dissolve 8.2 g anhydrous sodium acetate in glacial acetic acid (300 ml) and dilute to 1 litre. Standardize against perchloric acid in the same solvent.

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Indicators. Either Crystal Violet, 0.5% in glacial acetic acid (blue, through blue-green to green), or Oracet Blue B, 0.5% in glacial acetic acid (blue, through purplish to pink) suitable.

Procedure

Method 1. A weight of sample containing an estimated 0.3-0.4 milliequivalents of titratable nitrogen was boiled gently with 20 ml of glacial acetic acid for about one minute. This treatment usually caused considerable swelling and degradation of the resin. The contents of the flask were allowed to cool, one drop of indicator added and 0.1*N* perchloric acid in glacial acetic acid run in until the indicator changed colour. The flask was then placed in an air oven maintained at approx. 100°C. When the original colour of the indicator returned, a further addition of perchloric acid was made, this process being repeated until a permanent end-point colour was obtained. Almost invariably, it was observed that if the solution did not change colour within an hour at 100°C then the end-point had been reached. As a check the flasks were left overnight at 40° when no further colour change should be observed.

Method 2. A similar weight of sample was mixed with perchloric acid in acetic acid (5.00 ml of 0.1*N* solution) and glacial acetic acid (10 ml) in a stoppered flask which was then placed in the air oven at 100° for 24 hours. The resin was then filtered off and washed with 35 ml of hot acetic acid. Two drops of indicator solution were added to the combined filtrate and washings and the solution was back titrated with 0.1*N* sodium acetate solution in glacial acetic acid.

It was pertinent with respect to both methods that the stability of perchloric acid solutions at 100°C should be examined. It was, in fact, little affected by heating at 100° for 24 hours. A solution having an initial titre of 4.87 ml of freshly standardized sodium acetate solution had, after this treatment, a titre of 4.83 ml. Correction for this almost insignificant change is unnecessary within the limits of accuracy of the method.

RESULTS

The results, which for both methods are considered to be ± 5% in error are tabulated below, together with the equivalent calculated from the ultimate nitrogen analysis (Micro Dumas) or by conventional aqueous titration methods.

TABLE I

Type of resin	*Equivalent by titration method* *I*	*II*	*Equivalent from nitrogen analysis*
Primary amine	315		325
	400	315	360
		1370	1380
	655		636
(Polyaminostyrene)	147		156*
	149		156*
Secondary amine	495		505
	750		735
Tertiary amine	285	305	300
	610		620
Imine (Schiff's base)	250	220	245
	240		235
	435	370	425
Amino-phosphonate	750		735
Carboxylic acid (Na salt)	190		195**
Phosphonic acid (Na salt)	345		353***

* Titration with 0.1*N* $NaNO_2$. ** Titration with 0.1*N* NaOH. ***From P analysis

DISCUSSION

Method 1 generally gives a value for the equivalent of the resin in agreement with that derived from ultimate analysis. The second method generally gives lower values. Sometimes, this discrepancy is serious and no obvious reason for it, except

References p. 209

possibly oxidation is apparent. Retention of perchloric acid solution by the resin would account for only a small fraction of the error. Accordingly, the first method, although more time-consuming, is the more reliable.

The method is applicable to a range of basic nitrogenous resins and has been of particular use for the determination of the extent of replacement or insertion of basic groups into synthetic resin matrices, especially for the reduction of polynitrostyrene to polyaminostyrene by various treatments. Here, a nitrogen analysis does not give an adequate indication of the amount of amino nitrogen present, and this is valid for a number of reactions which only partly proceed to completion.

It may also be used to determine the alkali metal content of conventional carboxylic acid and phosphonic acid resins and we anticipate that any resin will be titratable by this method provided it contains a grouping that may be successfully titrated by this method when in monomeric form. In the case of metals other than the alkali metals there may be some interaction with the perchloric acid. This has been investigated by PIFER AND WOLLISH[3] for several metal salts and the results may be applicable to resin matrices containing these particular metals.

SUMMARY

A non-aqueous titrimetric procedure is described for the determination of basic functional groups in ion exchange resins.

RÉSUMÉ

Une méthode titrimétrique, en milieu non-aqueux, est décrite pour le dosage des groupements fonctionnels basiques des résines d'échange d'ions.

ZUSAMMENFASSUNG

Die Verfasser beschreiben eine titrimetrische Methode, in nicht-wässrigem Milieu, zur Bestimmung der basischen funktionellen Gruppen in Ionenaustauscherharzen.

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ZUR DIREKTEN TITRATION ORGANISCHER VERBINDUNGEN MIT CHROM(II)SULFAT

von

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Im Gegensatz zu Titan(III)chlorid, dessen Reduktionspotential zur direkten Titration kaum ausreicht, lassen sich zahlreiche organische Gruppen mit Chrom(II)-sulfat direkt elektrometrisch titrieren.

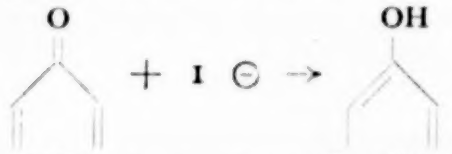
Viele Verbindungen, oft sogar Isomere, zeigen grosse Unterschiede im Redoxpotential. Somit lassen sich zahlreiche Gruppen und Isomeren ***nebeneinander*** quantitativ, oft auch qualitativ bestimmen.

Die Titration von Kationen nebeneinander ist schon beschrieben worden[1].

Reaktionen

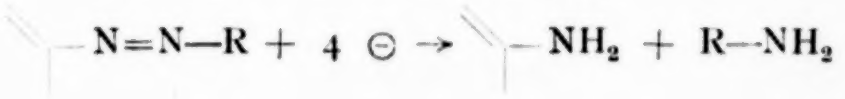
Grundreaktion: $Cr^{+2} - 1\ \ominus \rightarrow Cr^{+3}$

$(H_2O + 1\ \ominus \rightarrow H + OH^-)$



$R{-}NO + 4\ \ominus \rightarrow R{-}NH_2$

$R{-}NO_2 + 6\ \ominus \rightarrow R{-}NH_2$



$-N{=}N{-}R + 4\ \ominus \rightarrow -NH_2 + R{-}NH_2$

EXPERIMENTELLES

Herstellung der Chrom(II)sulfatlösung

Das Reagens kann elektrolytisch[2] oder durch Reduktion mit Zink erhalten werden. Wir arbeiten meist nach der Angabe von ZINTL UND RIENÄCKER[3]:

Kaliumbichromat wird mit conc. Salzsäure zur dreiwertigen und anschliessend mit Zink zur zweiwertigen Stufe reduziert. Nun wird das zweiwertige Chrom als Acetat gefällt, filtriert, gewaschen und in *ca.* 1-normaler Schwefelsäure gelöst, sodass eine etwa 0.1-normale Chrom(II)-Lösung entsteht.

Titrationseinrichtung

Die Titrationsapparatur muss vollkomen luftdicht sein, das Reagens darf nur mit sauerstofffreiem Stickstoff bewegt werden (Reinigung des Stickstoffs[4]). Der oben plangeschliffene Becher wird mit Federn gegen einen Polyäthylendeckel gepresst, der Löcher zur Aufnahme der Bürette, der Elektroden, des Stickstoffeinleitungsrohres und eines Thermometers trägt. Zur Aufbewahrung der Lösung eignen sich am besten Wulff'sche Flaschen. Als Indikatorelektrode dient eine blanke Plantinelektrode, als Vergleichselektrode eine gesättigte Kalomelelektrode, die über einen Agar-Agar-Heber mit dem System verbunden ist. Zur Potentialmessung kann jedes direktzeigende oder kompensierende mV-Gerät verwendet werden.

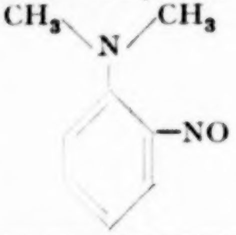
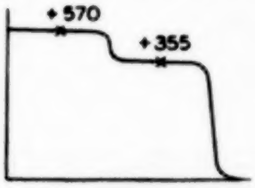
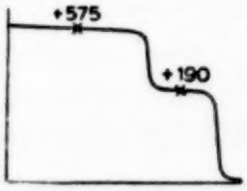
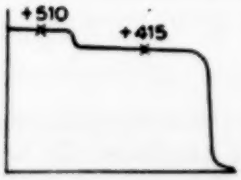
Literatur S. 213

Ausführung der Titration

Man löst 50-500 mg Substanz in Wasser, Dimethylformamid, Pyridin oder verdünnter Schwefelsäure, bringt mit 1-normaler-Schwefelsäure auf 50 ml und titriert mit Chrom(II)sulfat. Man gibt stets gleiche Mengen Chromlösung zu, wartet Potentialkonstanz ab und trägt das Resultat graphisch auf.

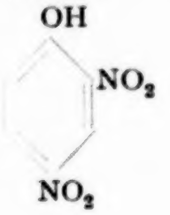
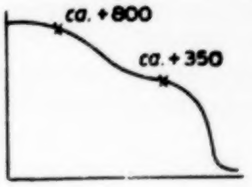
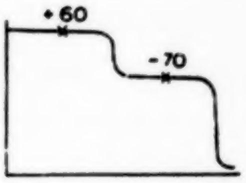
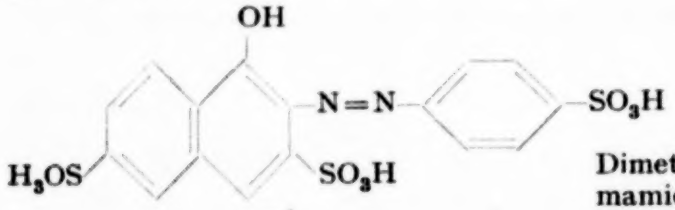
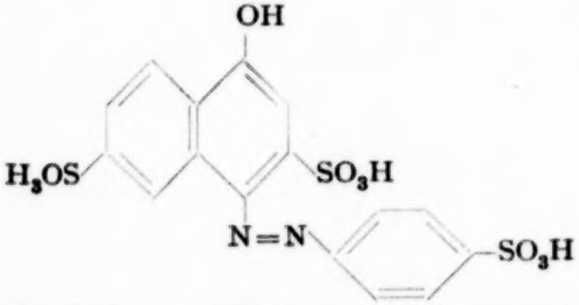
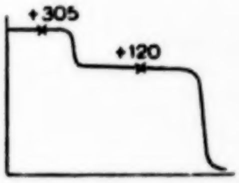
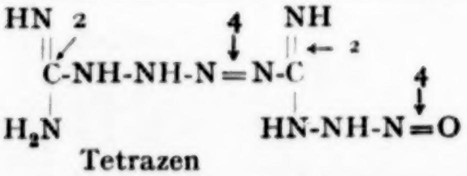
Die Messung des pH erfolgt mit einer Glaselektrode; bei der Auflösung in Stufen bei der Anwesenheit mehrerer reduzierbarer Gruppen ist die Einhaltung des pH (Pufferung) zu beachten.

*Beispiele**

Verbindung	*Verbrauch Äquivalente Cr^{+2}*	*Lösungsmittel*	*Redoxpotential mV Kurve*	*mittl. Abweichung v. Sollwert*
p-Chinon	2	Wasser	+ 205	± 0.5 %
Anthrachinon-2-sulfosäure	2	H_2SO_4 *N*	+ 170	± 0.8 %
Anthrachinon-2.7-disulfosäure	2	H_2SO_4 *N*	+ 255	± 0.5 %
p-Nitrosophenol	4	H_2SO_4 *N*	+ 535	± 0.5 %
o-Nistrosodimethyl-anilin 	4	H_2SO_4 *N*	+ 355	± 1.2 %
p-Nitrosodimethylanilin	4	H_2SO_4 *N*	+ 565	± 0.8 %
Gemisch 1 : 1 *o*-Nitrosodimethylanilin und *p*-Nitrosodimethylanilin	4	H_2SO_4 *N*		*o* : ± 2% *p* : ± 1.3%
1-Nitroso-2-naphtol	4	H_2SO_4 *N*	+ 575	± 1 %
3-Nitroso-2-naphtol	4	H_2SO_4 *N*	+ 190	± 2 %
Gemisch 2 : 1 1-Nitroso-2-naphtol und 3-Nitroso-2-naphtol	4	H_2SO_4 *N*		1-Nitroso : ± 1.6 % 3-Nitroso : ± 2.5 %
o-Nitrophenol	6	Eisessig/H_2O /Na-acetat pH = 2	+ 415	± 1 %
p-Nitrophenol	6	Eisessig/H_2O /Na-acetat pH = 2	+ 510	± 2.5 %
Gemisch 2 : 1 *o*-Nitrophenol und *p*-Nitrophenol	6	Eisessig/H_2O /Na-acetat pH = 2		*o* : ± 3 % *p* : ± 5 %

* Alle Potentiale gegen gesättigte Kalomelelektrode gemessen

Literatur S. 213

Verbindung	*Verbrauch Äquivalente Cr^{+2}*	*Lösungsmittel*	*Redoxpotential mV Kurve*	*mittl. Abweichung v. Sollwert*
m-Dinitrophenol 	12	Pyridin/H_2O/H_2SO_4 pH = 2		1. Stufe : ± 10 % 2. Stufe : ± 10 %
		Pyridin/H_2O/H_2SO_4 pH = 7		1. Stufe : ± 5 % 2. Stufe : ± 3 %
Pikrinsäure	18	Eisessig/H_2O bei 40°C	+ 390	± 1.5 %
Trinitrotoluol	18	Dimethylformamid/H_2SO_4 2*N* bei 40°C	+ 560	± 3 %
Gemisch 2 : 1  und 	4	Dimethylformamid, H_2O und H_2SO_4 *N* 40% : 30% : 30%		1. Stufe: ± 10 % 2. Stufe : ± 7 %
 Tetrazen	12	Dimethylformamid H_2SO_4 2*N*	+ 465	± 1.5 %
Aminoazobenzol	4	Dimethylformamid H_2SO_4 2*N*	+ 340	± 2.5 %

ZUSAMMENFASSUNG

Azo, Nitro-, Nitroso-und Chinongruppen wurden mit Chrom(II)sulfat direkt elektrometrisch titriert. In vielen Fällen konnte die Stellung der Gruppen durch ihr Redoxpotential unterschieden und diese Gruppen nebeneineinander bestimmt werden.

SUMMARY

Azo-, nitro-, nitroso- and quinoid groups can be determined directly by electrometric titration with chromium(II) sulphate. In several cases isomeres have different redox potentials, consequently they give different steps in the titration curve and can be determined without separation.

Literatur S. 213

RÉSUMÉ

Les groupements azo-, nitro, nitroso- et quinoïdes peuvent être dosés directement par titrage électrométrique, au moyen de sulfate de chrome(II). Dans de nombreux cas, des isomères ont des potentiels rédox différents, ce qui permet de les doser les uns en présence des autres.

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ESTIMATION OF FLUORINE IN MICROGRAMME QUANTITIES
A MODIFIED PROCEDURE

by

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INTRODUCTION

The estimation of traces of fluorine occurring in various types of materials such as ores, slags, dusts, plant products, *etc.*, has assumed considerable importance in recent years. The most widely used method for this purpose is the Willard-Winter distillation of the material with steam in the presence of sulphuric or perchloric acid[1,2]. Fluorine distills over quantitatively as hydrofluosilicic acid which is subsequently titrated against standard thorium nitrate solution with alizarin or solochrome blue as indicators[3,4,5]. In this distillation it is not possible to prevent entirely the carry over of traces of either the acid used or the acid radicals present in the sample, some of which interfere seriously with the subsequent titration. The usual procedure[6] for overcoming this difficulty has been to concentrate the distillate and redistill it with perchloric acid, the carry over of which is usually much lower than the amount that affects the accuracy of the titration.

Our preliminary observations showed, and this is also supported by earlier work[1,7], that the presence of large excesses of silica, alumina and iron exerts a distinct retarding influence on the rate of disintegration of the samples and the volatilization of fluorine. This effect is much less pronounced with sulphuric or phosphoric acid than with perchloric acid. An attempt was, therefore, made to adopt the sulphuric acid or phosphoric acid distillation to yield reliable values for fluorine without having recourse to either a second distillation, or the use of perchloric acid which is rather hazardous.

References p. 215

EXPERIMENTAL

The apparatus employed for the steam distillation was similar to that described by the BRITISH MEDICAL RESEARCH COUNCIL[8], with the improvement that the side-arm of the flask carrying the splash-head was made wider and bent upwards to prevent the blocking of the tube by condensed vapour, thereby reducing the entrainment of the liquid to a minimum. Before use, new equipment was always subjected to a thorough preliminary treatment as follows: Continuous steam-distillation was carried out in the presence of a sufficient quantity of acid, until the blank was reduced to a value lower than 0.05 ml of 0.004*N* thorium nitrate solution. It may incidentally be mentioned that the apparatus need not necessarily be of Pyrex glass, as our experience has clearly shown that other varieties of glass serve the purpose equally well. The use of glass wool[8] was dispensed with, as it caused high and uncertain blanks.

Two grams of the sample were taken in the distillation flask and distilled water added to give a total volume of approximately 25 ml. When larger volumes of fluoride solutions were employed, they were made alkaline before being concentrated to 25 ml. Forty ml of the acid to be used was then added through the thistle funnel and the contents steam-distilled at 135-140° C. The distillate was collected in a receiver containing 10 ml of *N*/10 sodium hydroxide solution, taking care to see that the tip of the condenser dips into the liquid.

The interference due to PO_4^{-3} and SO_4^{-2} ions in the distillate was eliminated in the following manner: 1% silver nitrate solution was run into the distillate dropwise, until no further precipitation was noticed, and the mixture was warmed gently and filtered. The filtrate was then treated with excess *N*/10 baryta solution, filtered again and made up to a known volume (250 ml). In all cases of filtration, scrupulous care should be taken to avoid the use of brands of paper which are subjected to hydrofluoric acid treatment in their manufacture. Although, in the above procedure, ideal conditions have not been adopted for effecting the precipitation, the separation of the ions was sufficiently satisfactory to reduce their concentration well below the limits of interference.

An aliquot from the above solution was titrated according to the procedure described by ARMSTRONG[3], HOSKINS AND FERRIS[4], and MILTON, LIDDELL AND CHIVERS[5]. We have, however, found it more advantageous to employ 0.2*N* chloracetic acid instead of 1.0*N* perchloric acid for neutralizing the alkaline distillate before treatment with the buffer solution.

The above procedure was applied to the estimation of fluorine in a large number of synthetic samples, covering a wide variety of composition, and the results are presented in Table I. An examination of this clearly shows that the sulphuric acid or phosphoric acid method compares favourably in regard to the accuracy attainable with the perchloric acid method. Further, from the data incorporated in Table II, it will be obvious that the technique employing sulphuric or phosphoric acid is simpler in that comparatively smaller volumes are required for effecting a quantitative carry over of the fluorine.

It may thus be stated that the modified procedure described in this paper, which obviates the use of perchloric acid has the advantage of improved safety and increased simplicity.

The authors' thanks are due to the Management of the Tata Iron and Steel Co., Ltd., for permitting the publication of this paper.

TABLE I

ESTIMATION OF FLUORINE USING $HClO_4$, H_2SO_4 AND H_3PO_4 FOR DISTILLATION

Fluorine content (μg)	*Fluorine recovered (μg)* *$HClO_4$ distn.*	 *H_2SO_4 distn.*	 *H_3PO_4 distn.*
50	45	55	50
125	125	125	125
250	250	245	250
375	345	370	360

TABLE II

VOLUME OF DISTILLATE COLLECTED FOR EFFECTING COMPLETE RECOVERY OF FLUORINE

Fluorine content (µg)	*Volume of distillate (ml)*		
	$HClO_4$ distn.	*H_2SO_4 distn.*	*H_3PO_4 distn.*
50	200	200	200
125	200	200	200
250	500	200	400
375	600	400	500

SUMMARY

A procedure is described for the estimation of fluorine in microgramme quantities by the steam-distillation of the samples with sulphuric or phosphoric acid. Traces of the acid carried over are precipitated from the distillate as silver or barium salts, in order to eliminate their interference in the subsequent titration of fluorine. The results obtained compare favourably with those of the conventional perchloric acid method. By avoiding the latter, the present method offers the advantage of both safety and simplicity.

RÉSUMÉ

Une méthode est décrite pour le dosage de microquantités de fluor par traitement de la substance à analyser à l'acide sulfurique ou à l'acide phosphorique et distillation par entraînement à la vapeur. Les traces d'acide entraînées sont séparées du distillat par précipitation des sels d'argent ou de baryum, pour éviter que ces acides gênent lors du titrage du fluor. Les résultats obtenus sont satisfaisants comparés à ceux de la méthode habituelle à l'acide perchlorique. La méthode proposée présente l'avantage d'être à la fois sûre et simple.

ZUSAMMENFASSUNG

Ein Verfahren zur Bestimmung von Mikrogramm-Mengen Fluor durch Dampfdestillation der Proben in Gegenwart von Schwefelsäure oder Phosphorsäure wird beschrieben. Mitgerissene Spuren von Säuren müssen im Destillat als Silber- oder Bariumsalze gefällt werden, da sie sonst die Fluortitration stören. Die Ergebnisse sind im Vergleich zu denen der üblichen Perchlorsäure-Methode befriedigend. Die Vorteile der neuen Methode sind Zuverlässigkeit und Einfachkeit.

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THE GRAVIMETRIC DETERMINATION OF THALLIUM(I) AS THALLIUM(I) TETRAPHENYLBORON

by

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A great amount of research has been conducted during the past 25 years on the detection and quantitative estimation of thallium. A review of the literature on the analytical chemistry of this element has recently been written by **ANDERSON**[1].

It was observed by **WITTIG AND RAFF**[2] that thallium(I) was quantitatively precipitated by the tetraphenylboron ion $[B(C_6H_5)_4]^-$ as $Tl[B(C_6H_5)_4]$. **GEILMANN**[3], using ^{204}Tl as a tracer, determined the solubility of this compound to be 5-6 γ/100 ml. Using this reagent, a new gravimetric determination for thallium(I) was developed which offered the advantages of a very insoluble precipitate, limited interferences by other metal ions, sufficient thermal stability so that the precipitate could be weighed directly and having a favorable gravimetric factor (35.63% thallium compared to 77.89% thallium in Tl_2CrO_4).

EXPERIMENTAL

Reagents

Sodium tetraphenylboron was obtained from the J. T. Baker Chemical Co., Phillipsburg, N. J. Thallium(I) chloride, purified, was obtained from the Fisher Scientific Co., New York, N. Y. All other chemicals were of reagent grade quality.

Solutions

Sodium tetraphenylboron solution. Dissolved 2.0 g of sodium tetraphenylboron in 100 ml of doubly distilled water. To this were added 0.5 ml of 1*M* $Al(NO_3)_3$ solution and 0.5 ml of 1*M* NaOH solution. The resulting cloudy solution was filtered through a sintered porcelain crucible and stored in a glass bottle.

Sodium acetate solution, 2*M*.

Aerosol solution, 0.1% (w/v).

Standard thallium(I) sulfate solution. Approximately 2.5 g of thallium(I) chloride was dissolved in 3 ml of concentrated H_2SO_4, heated to expel the resulting HCl, and made up to 1 liter in a volumetric flask. The thallium solution was standardized by the chromate method[4].

Thermobalance

The procedure used in the thermogravimetric pyrolysis and the operation of the thermobalance has previously been described[5].

Precipitation procedure

The following procedure was used to precipitate thallium as thallium(I) tetraphenylboron. An aliquot (containing from 0.0166 to 0.0416 g of thallium) of the standard thallium solution was pipetted into 400 ml beakers. To this solution were added 40 ml of water, 20 ml of 2*M* sodium acetate solution and 2 drops of aerosol solution. The thallium was precipitated at room temperature by adding a slight excess of 2% sodium tetraphenylboron solution (usually 3 to 8 ml were required). Immediately a flocculent white precipitate formed which slowly settled to the bottom of the beaker on standing for about two hours. The precipitates were filtered into tared porcelain crucibles, using suction, washed three times with 10 ml portions of water and dried in an air oven at 100 to 105°C for four hours.

Effect of acidity on precipitation

The procedure was the same as in the previous part except that the concentration of acid was adjusted with concentrated sulfuric acid. Nitric acid in concentrations greater than 1*N* caused oxidation of the thallium precipitates.

Qualitative reaction of tetraphenylboron ion with metal ions

To a 5 ml solution containing about 100 mg of the metal salt were added 0.10 ml of 6*N* HNO_3 and 1.0 ml of 2% sodium tetraphenylboron solution. The resulting solution was allowed to stand 30 minutes before recording the results.

TABLE I

EFFECT OF ACID CONCENTRATION ON THE PRECIPITATION OF THALLIUM(I)

H_2SO_4 concentration	Thallium found g	Thallium theor. g	Deviation g
0.01*N*	0.0260	0.0260	0.0000
1.0*N*	0.0257	0.0260	—0.0003
2.0*N*	0.0256	0.0260	—0.0004
3.0*N*	0.0255	0.0260	—0.0005
4.0*N*	0.0250	0.0260	—0.0010
5.0*N*	0.0248	0.0260	—0.0012

DISCUSSION AND RESULTS

Effect of acidity on precipitation

The effect of acid concentration on the precipitation of thallium(I) is shown in Table I. It can be seen that a concentration of acid in excess of 1*N* caused a fairly large error in the determination. At 5*N* acid concentration, the loss of thallium was about four times greater than that at 0.01*N*. The solubility of the precipitate increased with an increase in acid concentration. Strong nitric acid solution exerted an oxidizing action on the thallium precipitates so that it should not be used in greater than 1*N* concentrations. Hydrochloric acid would, of course, cause precipitation of thallium(I) chloride. It appears that the best precipitating conditions require an acid concentration below 1*N*.

Thermolysis of thallium(I) tetraphenylboron

The thermal decomposition curve of thallium(I) tetraphenylboron is shown in Fig. 1. The air dried precipitate was stable up to 180°C where it began to decompose slowly. At 200°C the rate of decomposition increased, resulting in a mixture containing some carbonaceous matter at 325°C. The carbonaceous matter oxidized slowly giving at 450°C a mixture of $TlBO_2$ and some Tl_2O_3. This mixture was stable up to 700°C where it began to volatilize from the thermobalance pan. It is obvious from the thermal decomposition curve that the precipitate cannot be ignited to pure thallium metaborate or thallium(III) oxide. However, there is certainly no need of this because the precipitated compound is sufficiently stable as to be weighed directly.

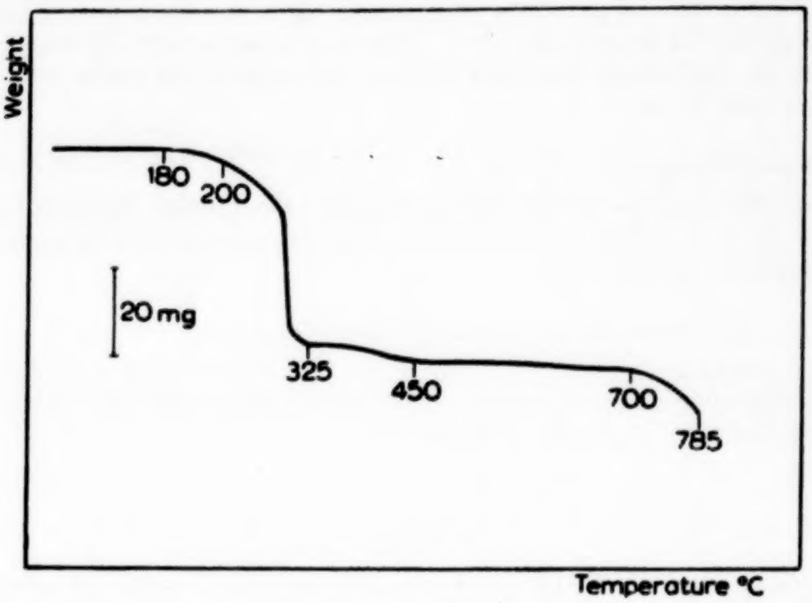

Fig. 1. The thermal decomposition of thallium(I) tetraphenylboron.

Reaction of the tetraphenylboron ion with metal ions

Because of the widely adopted use of the tetraphenylboron method for the determination of potassium, several studies have been concerned with the interference of other metal ions in the determination. Rudorff and Zannier[6] found that iron(III) gave a dark iron colored precipitate with the reagent. The most comprehensive study of interfering ions was made by Sporek and Williams[7]. They found that the metal ions of Ce(IV), Cu(I), Hg(II), Ag(I) and Th(IV) gave precipitates with the reagent. The ions of Hg(II) and Th(IV) appeared to be quantitatively precipitated but the composition of the precipitated compounds was not reported.

The results of the qualitative tests with 33 metal ions differ from previous investigators and are shown in Table II. It is seen that K, Rb, Zn, Cs, Hg(I), Hg(II), Ag, Ce(IV), Zr, Co(II), Ni, Mn(II), Pt(IV), Sb(III), Bi(III) and NH_4 ions all formed precipitates with the tetraphenylboron ion. However, on studying these precipitates on the thermobalance it was found that the precipitates with Zn, Ce(IV), Zr, Sb(III), Co(II), Ni, Mn(II) and Bi(III) did not contain any metal. The precipitates decomposed on the thermobalance but did not leave any residues. Apparently, the acid in the solution must react with the sodium tetraphenylboron according to the following equations[7]:

$$Na[B(C_6H_5)_4] + H^+ \rightarrow B(C_6H_5)_3 + Na^+ + C_6H_6$$

$$B(C_6H_5)_3 + 2\ H_2O \rightarrow C_6H_5\ B(OH)_2 + 2\ C_6H_6$$

It was found that the precipitates did not form immediately on adding the reagent but appeared after standing 10-15 minutes. However, K, Rb, Cs, Hg(I), Hg(II), Ag and NH_4 formed precipitates with the reagent immediately on mixing. Thorium did not give a precipitate as previously described.

Sporek and Williams[7] found that potassium could be determined by the tetraphenylboron method even though Co(II), Ni, Fe(III), Mn(II) and other metal ions were present. Yet, these same metal ions, in an acid solution, caused the formation

TABLE II

REACTION OF SODIUM TETRAPHENYLBORON WITH VARIOUS METAL IONS

Metal	*Metal salt*	*Results*
Lithium	$LiNO_3$	N. R.
Potassium	KCl	White ppt.
Rubidium	$RbCl$	White ppt.
Cesium	$CsCl$	White ppt.
Magnesium	$Mg(NO_3)_2 \cdot 6H_2O$	N. R.
Calcium	$Ca(NO_3)_2 \cdot 4H_2O$	N. R.
Strontium	$Sr(NO_3)_2$	N. R.
Barium	$Ba(NO_3)_2$	N. R.
Zinc	$Zn(NO_3)_2 \cdot 6H_2O$	White ppt.
Cadmium	$Cd(NO_3)_2 \cdot 6H_2O$	N. R.
Mercury(I)	$HgNO_3 \cdot H_2O$	Grey ppt.
Mercury(II)	$Hg(NO_3)_2 \cdot xH_2O$	White ppt.
Silver	$AgNO_3$	White ppt.
Yttrium	$YCl_3 \cdot 6H_2O$	N. R.
Lanthanum	$LaCl_3 \cdot 6H_2O$	N. R.
Cerium(III)	$CeCl_3 \cdot 6H_2O$	N. R.
Cerium(IV)	$Ce(HSO_4)_4$ in $6N$ H_2SO_4	White ppt.
Aluminum	$Al(NO_3)_3 \cdot 9H_2O$	N. R.
Uranium(VI)	$UO_2(NO_3)_2 \cdot 6H_2O$	N. R.
Thorium	$Th(NO_3)_4 \cdot 4H_2O$	N. R.
Zirconium	$ZrOCl_2$	White ppt.
Tin(II)	$SnCl_2 \cdot 2H_2O$	N. R.
Lead	$Pb(NO_3)_2$	N. R.
Iron(III)	$Fe(NO_3)_3 \cdot 9H_2O$	N. R.
Cobalt(II)	$Co(NO_3)_2 \cdot 6H_2O$	White ppt.
Nickel	$Ni(NO_3)_2 \cdot 6H_2O$	White ppt.
Chromium	$Cr(NO_3)_3 \cdot 9H_2O$	N. R.
Copper(II)	$CuCl_2 \cdot 2H_2O$	N. R.
Manganese(II)	$MnCl_2$·aq. soln.	White ppt.
Platinum(IV)	$H_2[PtCl_6]$ (5% soln.)	White ppt.
Antimony(III)	$SbCl_3$ in $6N$ HCl	White ppt.
Bismuth(III)	$BiONO_3$ in $6N$ HNO_3	White ppt.
Ammonium	NH_4Cl	White ppt.

Note: N. R. — no reaction.

of a precipitate of $C_6H_5B(OH)_2$ while with other metal ions, in the same acid concentration, no precipitates were formed.

The formation of insoluble compounds with the tetraphenylboron ion suggests that perhaps other metals could be determined as the tetraphenylboron compound. Judging from these qualitative results, the only metal which it is felt could easily be determined analytically would be mercury(II). A flocculent white precipitate was obtained which rapidly settled to the bottom of the test tube on standing. The precipitation appeared quantitative.

Results of analysis

The results of the precipitation of thallium(I) as thallium(I) tetraphenylboron are shown in Table III. The results obtained show that the errors in the determination are largely within the experimental limit and compares favorably with the classical chromate method.

TABLE III

THE PRECIPITATION OF THALLIUM AS THALLIUM(I) TETRAPHENYLBORON

Exper. No.	*Thallium found* g	*Thallium theor.* g	*Deviation* g
1	0.0419	0.0416	+0.0003
2	0.0418	0.0416	+0.0002
3	0.0415	0.0416	—0.0001
4	0.0414	0.0416	—0.0002
5	0.0416	0.0416	0.0000
6	0.0250	0.0250	0.0000
7	0.0251	0.0250	+0.0001
8	0.0253	0.0250	+0.0003
9	0.0251	0.0250	+0.0001
10	0.0165	0.0166	—0.0001
11	0.0167	0.0166	+0.0001
12	0.0167	0.0166	+0.0001
13	0.0167	0.0166	+0.0001
14	0.0258	0.0260	—0.0002
15	0.0258	0.0260	—0.0002
16	0.0260	0.0260	0.0000
17	0.0258	0.0260	—0.0002
18	0.0259	0.0260	—0.0001

ACKNOWLEDGEMENT

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SUMMARY

A gravimetric method for the determination of thallium(I) as thallium(I) tetraphenylboron has been developed. The method compares favorably with the classical chromate method. The effect of acid concentration and interference by other metal ions was studied as well as the thermal stability of the precipitate.

RÉSUMÉ

Une méthode gravimétrique est proposée pour le dosage du thallium(I) à l'état de thallium(I) tétraphénylbore. Ce procédé est avantageux par rapport à la méthode classique au chromate. L'effet de la concentration en acide et l'influence d'autres ions métalliques ont été étudiés. Un examen de la stabilité thermique du précipité a également été effectué à l'aide de la thermobalance.

ZUSAMMENFASSUNG

Eine gravimetrische Methode zur Bestimmung von einwertigem Thallium als Thallium(I) Tetraphenylbor wurde entwickelt. Die neue Methode bietet Vorteile im Vergleich zur klassischen Chromatmethode. Der Einfluss der Säurekonzentration und von anderen Metallionen wurde studiert; ausserdem wurde die Hitzebeständigkeit des Niederschlages mit Hilfe der Thermowaage untersucht.

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SUR LA STABILITÉ THERMIQUE DES ÉTALONS ANALYTIQUES. IV*

par

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Dans cette quatrième série, nous présentons une étude relative aux 12 corps suivants: hydroxyde de sodium, thiosulfate de sodium, émétique, chlorure d'étain(II), acide oxalique, nitrate d'argent, sulfate de cuivre, nitrate de bismuth, acide iodique, chlorate de potassium, métavanadate d'ammonium, acide sulfamique.

Toutes ces substances ont été chauffées sur l'une des thermobalances à enregistrement photographique, avec échauffement linéaire à raison de 300° par heure et avec des poids de substance de l'ordre de 200 mg. Les spectres infrarouges ont été réalisés sur poudre, avec vaseline comme agglomérant, entre 6 et 15 μ, sur le spectromètre Perkin-Elmer 12C avec optique de sel gemme.

Hydroxyde de sodium

Nous avons utilisé un flacon de soude caustique en lentilles, Merck. Le produit commence par gagner de l'humidité jusque vers 94° (Fig. 1) puis on retombe sur un corps sensiblement anhydre entre 150 et 337° où le produit est alors fondu. Ensuite s'échappe l'eau de constitution et, au-dessus de 480°, s'étend un nouveau palier horizontal correspondant à l'oxyde basique Na_2O qui reste stable jusqu'à 980°, limite de notre expérience.

Le spectre infrarouge effectué sur l'hydroxyde de sodium non-carbonaté soit à l'état sec, soit à l'état de solution, ne donne évidemment pas de bande dans la région étudiée.

Thiosulfate de sodium

Le thiosulfate de sodium ne conserve ses 5 molécules d'eau que jusqu'à 37° (Fig. 2). Déjà à 47°, la perte se manifeste. Un court palier vers 114° correspond à peu près au départ de deux molécules d'eau. Un palier légèrement incliné, beaucoup plus long, s'étend de 215 à 387° et s'accorde à peu près avec le produit anhydre. La décomposition se manifeste alors brutalement à 475°. Le résidu renferme surtout du sulfate de sodium et des quantités variables de sulfite et de sulfure sans qu'il soit possible d'écrire une équation unique.

Le spectre infrarouge du sel pentahydraté montre une bande très forte pour 999 cm^{-1} qui coïncide avec la bande polarisée très forte du spectre Raman et qui correspond à la vibration ν_1 déplacée des sulfates, spectre en accord avec ceux déjà obtenus par R. DUVAL ET J. LECOMTE[1]. Cette bande large correspondant à ν_1 se trouve également en solution aqueuse à 995 cm^{-1}. De plus, nous avons trouvé en solution aqueuse une autre bande très forte à 1117 cm^{-1} qui apparaît difficilement avec le solide et qui correspond au mode de vibration ν_{2-3} et à la bande dépolarisée du spectre Raman.

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* Pour le troisième mémoire de cette série, voir *Anal. Chim. Acta*, 15 (1956) 223.

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Bibliographie p. 225

Émétique

Nous sommes partis d'un produit anhydre qui se montre stable jusqu'à 149° (habituellement le semi-hydrate utilisé en médecine se déshydrate à 100°). Une molécule d'eau de constitution disparaît lentement entre 149 et 250° et l'anhydride interne de Bougault se montre suivant un palier horizontal se prolongeant jusqu'à 334° (Fig. 3). Alors se produit une explosion; la matière organique brûle et il reste, comme l'on sait, au-dessus de 540°, l'alliage de Serullas. Il est donc possible en vue de confectionner une liqueur titrée, de peser le semi-hydrate du commerce, le produit anhydre ou l'anhydride de Bougault.

Le spectre infrarouge déjà bien connu en dehors de nous, présente les bandes suivantes: 816 (aF), 825 (f), 853 (aF), 858 (aF), 888 (F), 921 (F), 925 (f), 1066 (f), 1076 (TF), 1133 (TF), 1234 (aF), 1268 (F), 1315 (aF), 1340 (F).

Chlorure d'étain(II)

Le chlorure d'étain(II) cristallisé avec deux molécules d'eau, ne les conserve en toute rigueur que jusqu'à 28°. Il se déshydrate progressivement jusqu'à 214° et le sel anhydre ainsi obtenu, se sublime presque aussitôt, en laissant au-dessus de 507° un oxychlorure d'une façon non-quantitative. La pesée de ce dihydrate pour faire une liqueur titrée, ne peut donner qu'une teneur approximative (Fig. 4).

Le chlorure d'étain(II) ne donne pas de bande d'absorption infrarouge et ne doit pas en donner dans la région du sel gemme.

Acide oxalique

L'acide oxalique pour analyses, sorti du flacon neuf, présente deux molécules d'eau qu'il conserve jusqu'à 38° (Fig. 5). La déshydratation se continue jusque vers 132° où un changement de direction dans la courbe indique que le produit anhydre, instable dans ces conditions, commence à se sublimer. A 231° le creuset est complètement vide. La préparation d'une liqueur titrée avec l'acide oxalique n'est donc pas tout à fait sûre à la suite d'une pesée des cristaux du dihydrate. L'oxalate de sodium est bien préférable comme nous l'avons déjà dit dans le troisième mémoire de cette série.

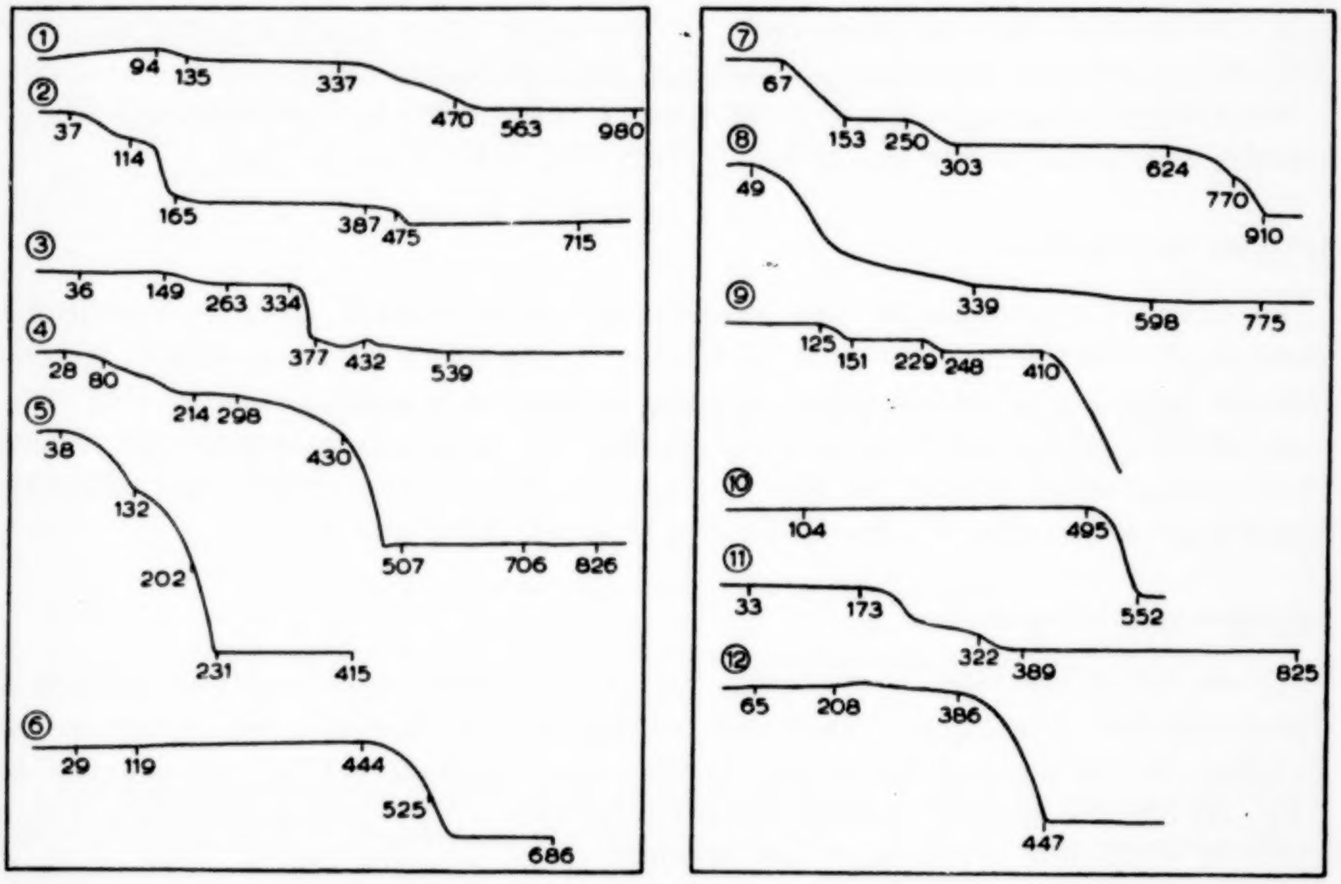
Le spectre infrarouge a été très étudié par DUVAL ET LECOMTE[2]. Nous retenons surtout dans la région du sel gemme, les bandes fortes pour 1116 et 1237 cm^{-1}.

Nitrate d'argent

Nous avons déjà donné une courbe de thermolyse du nitrate d'argent par comparaison avec celle du nitrate de cuivre, avec S. PELTIER[3]. Avec cette vitesse de chauffe, le nitrate d'argent se montre stable jusqu'à 444°, puis la décomposition se produit brusquement avec évacuation de vapeurs nitreuses jusqu'à 608° (Fig. 6).

Après quoi, on observe le palier horizontal de l'argent. Jusqu'à 444° nous n'avons pas observé de départ d'acide nitrique. La qualité analytique de ce sel offre des cristaux bien secs.

Le spectre infrarouge montre la bande forte correspondant au groupement NO_3 à 801 cm^{-1} et deux bandes très faibles pour 889 et 918 cm^{-1}.



Figs. 1-12.

Sulfate de cuivre

Le sulfate de cuivre se maintient stable avec 5 molécules d'eau jusqu'à 67° et l'on obtient un palier correspondant au monohydrate de 153 à 250° (Fig. 7). Il n'y a aucune évidence de l'apparition du semihydrate qui avait été signalé; à partir de 303° on obtient le palier du sel anhydre jusqu'à 624° et vers 747°, après départ de gaz sulfureux, on met en évidence le sulfate basique, jaune d'or, $2\,CuO.SO_3$. Finalement, après 910° commence le palier horizontal de l'oxyde CuO.

Le spectre infrarouge étudié à diverses reprises, nous a fourni sur le même échantillon les bandes suivantes: 1073 cm^{-1} (TF), 993 et 862 cm^{-1} (f).

Nitrate de bismuth

Il est très difficile d'utiliser ce sel comme étalon car il est hygroscopique et il commence à perdre de l'eau de cristallisation vers 49°. La courbe de thermolyse (Fig. 8) est très lentement décroissante et c'est seulement vers 600° que l'on arrive à l'oxyde Bi_2O_3.

Ce sel présente uniquement la bande caractéristique des nitrates pour 834 cm^{-1}.

Bibliographie p. 225

Acide iodique

L'acide iodique, corps anhydre, ne change pas de poids avec notre façon d'opérer avant 125° (Fig. 9). Une première perte d'eau se manifeste alors assez rapidement pour conduire à l'acide HI_3O_8 dont le palier s'étend entre 151 et 229°. Il n'y a aucune indication pour l'acide $H_2I_4O_{11}$ intermédiaire signalé par CHRÉTIEN. A 229° on observe une nouvelle perte d'eau s'achevant vers 248° et qui conduit à l'anhydride I_2O_5. On observe alors une dissociation et une sublimation rapide à partir de 410°. L'acide iodique peut donc être pesé tel quel en le prélevant du flacon.

Son spectre infrarouge qui a déjà été donné et interprété par d'autres expérimentateurs, a fourni les bandes suivantes: 755 (tf), 804 (aF), 1160 (F) cm^{-1}.

Chlorate de potassium

Le chlorate de potassium que nous avons utilisé, chauffé dans les conditions données plus haut, se montre stable jusqu'à 495°. L'oxygène se dégage ensuite progressivement jusqu'à 552° où commence le palier horizontal relatif au chlorure (Fig. 10).

Le spectre infrarouge de ce sel a été étudié avec un prisme à bromure de césium et un prisme de sel gemme par Mlle DUVEAU[4] et Mlle ROCCHICCIOLI[5]. On y relève les bandes suivantes: 479 (F), 619 (TF), 933 (F), 968 (TF), 989 (F).

Métavanadate d'ammonium

Ce sel est stable jusqu'à 173° (Fig. 11). Nous avions déjà chauffé ce sel pris à l'état humide[6]. Après quoi, l'ammoniac se dégage complètement. Nous mettons en évidence sur un court palier incliné l'acide métavanadique HVO_3, puis à partir de 389°, on observe le palier horizontal de l'anhydride V_2O_5. Cette courbe nous donne donc la possibilité d'effectuer correctement deux liqueurs titrées, l'une avec le produit initial, l'autre avec le produit final.

Le spectre infrarouge de ce sel offre deux bandes assez fortes à 847 et à 888 cm^{-1}, une bande faible à 938 et une forte à 1406 cm^{-1}.

Acide sulfamique

L'acide sulfamique, produit Prolabo recristallisé, se montre stable jusqu'à 186°; après quoi il se sublime et se décompose, le creuset étant vidé à 447° (Fig. 12).

Le spectre infrarouge de l'acide en poudre a été étudié par Mme T. DUPUIS[7], avec trois prismes respectivement: bromure de césium, chlorure de sodium, fluorure de lithium. Voici les bandes, 373 (F), 540 (F), 680 (F), 1007 (aF), 1061 (F), 1250 (F), 1291 (F), 1419 (F), 1519 (F).

RÉSUMÉ

Dans ce quatrième mémoire relatif aux étalons, nous avons tracé la courbe de thermolyse et donné le spectre d'absorption infrarouge sur solide de 12 substances pouvant servir à des titres divers à confectionner des liqueurs titrées en chimie analytique.

SUMMARY

In this fourth article on standards the authors have plotted the thermolysis curves and ascribed the infrared absorption spectra of 12 substances in the solid state. These substances can be used in various instances for making standard solutions for chemical analysis.

Bibliographie p. 225

ZUSAMMENFASSUNG

In dieser vierten Arbeit über Vergleichssubstanzen wurden die Thermolysekurven und Ultrarotspektren im festen Zustand von 12 Verbindungen bestimmt,welche in verschiedenem Masse zur Herstellung von analytisch-chemischen Titerlösungen dienen können.

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EXTENSION OF THE ISOTOPIC METHOD FOR THE DETERMINATION OF OXYGEN IN TITANIUM*

by

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The use of the isotopic method for the determination of oxygen in metals[1,2,3] has now been applied to titanium in the range of 0.04-0.2 wt. % O. This method is based on reacting a weighed sample of titanium metal mixed with a known amount of ^{18}O-containing "master alloy" in the *molten* state with graphite and liberating part of the oxygen as carbon monoxide. The $^{18}O/^{16}O$ ratio in the carbon monoxide is determined by a mass spectrometer.

Method of calculation

The percent oxygen, x, is calculated from the simple mixture rule, namely:

$$x = 100 \left[\frac{bt(m-n)}{an} - \frac{(cu-dv)}{a} \right]$$

where a = weight of sample;
b = weight of titanium "master alloy" containing t weight fraction oxygen, with m atom % of oxygen-18 in excess of the normal** isotopic concentration ($\cong$ 0.21 at. % ^{18}O);
c = weight of crucible containing u weight fraction oxygen;
d = weight of graphite containing v weight fraction oxygen;
n = atom % of oxygen-18 in excess of normal concentration *after* equilibrium.

Because isotopes are preferably mixed and measured on an atom per atom basis,

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** The exact normal isotopic concentration is determined before each series of analyses.

bt should be expressed either in gram-atoms or, more simply, in weight units using the same atomic weight of the element as in *a*. Thus *bt* is not expressed in actual milligrams of the heavy isotope, but in equivalent milligrams of the normal isotopic mixture (see Ref. 1, p. 760).

EXPERIMENTAL PART

Apparatus and procedure

The apparatus and procedure used were described in detail previously[1,2]. It was found recently[3] that by replacing the graphite crucible with a molybdenum one (made from 0.25 mm sheet metal), the oxygen blank correction can be reduced from about 3 mg down to 0.01 mg.

Samples analyzed

The titanium metal samples were supplied and analyzed by E. I. du Pont de Nemours & Co., and the Allegheny Ludlum Steel Company by the vacuum fusion method[4].

Experimental results

The data obtained by the isotopic method are tabulated and compared with those obtained by the vacuum fusion method in Table I. It is of interest that the vacuum fusion data are 10-15% lower than the isotopic values. This would indicate that in the vacuum fusion analyses not all of the oxygen has been liberated as carbon monoxide and that some of the oxygen is held by the metal. This concurs with the findings of HORTON AND BRADY[5] who recovered only 85-70% of the oxygen by the vacuum fusion method in the case of chromium. Similarly, RODGERS AND HARTER[6] using the same method, found that the recovery of nitrogen was not quantitative in analyzing zirconium metal. In their case the determination of nitrogen, in the form of ammonia, by the Micro-Kjeldahl method gave higher values than the vacuum fusion method.

TABLE I

DETERMINATION OF OXYGEN IN TITANIUM BY THE ISOTOPIC METHOD

(In all cases $m = 13.6762$ atom % ^{18}O, $t = 1.8917$ wt. % O and $u = v = 0.150$ wt. % O)

Substance	*DuPont*	*DuPont*	*Allegheny Ludlum Steel Company*	
	# 628	*# 507*	*# 2*	*# 3*
a, g weight of substance	1.80557	1.00844	2.22325	2.21545
b, g weight of master alloy	0.17860	0.13479	0.14674	0.15474
$c + d$, g weight of graphite	1.7273	2.04505	2.3285	2.2374
n, atom % ^{18}O above normal after equilibration	6.7534	4.9772	3.6417	3.7352
$m—n$	6.9228	8.6990	10.0345	9.9410
x = wt. % O in sample, observed	0.0483	0.1378	0.1870	0.2005
Wt. % O by vacuum fusion*	0.0436	0.1219	0.165	0.175
Difference, % of O content, isotopic-vacuum fusion	+9.7	+11.5	+11.8	+12.7

* Analyzed by supplier.

A possible error leading to a higher oxygen content by the isotopic method might be due to an exchange between oxygen-18 of the carbon monoxide and the oxygen-16 in the quartz. This error possibility, however, was shown in a previous publication[2], to amount to less than 0.5% of the actual oxygen content of the sample.

The only other way the isotopic method might give erroneously high results is if air leaks into the apparatus. This would immediately reveal itself by the appearance of atmospheric argon peaks in the mass analyses. However, no argon was found in any of our samples.

ACKNOWLEDGEMENTS

The authors wish to express their thanks to Dr. R. H. FLECKENSTEIN of the Du Pont Company and to Mr. W. A. PEIFER of Allegheny Ludlum Steel Company for supplying us with the titanium samples.

SUMMARY

Our method of isotopic elementary analysis has recently been applied to the determination of oxygen in metals. It is now extended to the determination of oxygen in titanium in the low range of 0.04 to 0.2 weight percent oxygen. The method has the great advantage that it gives quantitative results *without* a quantitative separation of oxygen in any form. In the samples analyzed it was found that the alternative vacuum-fusion method gives results which are 9-13% too low.

RÉSUMÉ

Notre méthode isotopique d'analyse élémentaire a été appliquée récemment au dosage de l'oxygène dans les métaux. Elle est appliquée maintenant au dosage de l'oxygène dans le titane, pour des teneurs de 0.04-0.2% en poids d'oxygène. Cette méthode présente le grand avantage de donner des résultats quantitatifs *sans* séparation quantitative de l'oxygène. Nous avons constaté que, pour les échantillons analysés, la méthode de fusion dans le vide donne des résultats 9 à 13% trop faibles.

ZUSAMMENFASSUNG

Vor kurzem wurde unsere Isotopen-Methode der Elementar-Analyse auf die Bestimmung von Sauerstoff in Metallen angewandt. Der Anwendungsbereich derselben wurde nunmehr auf die Bestimmung von Sauerstoff in Titan, in dem niederen Bereich von 0.04 bis 0.2 Gew. % Sauerstoff erweitert. Der grosse Vorteil der Methode ist darin zu erblicken, dass sie, *ohne* die quantitative Abtrennung des Sauerstoffes in irgendeiner Form zu erfordern, zu quantitativen Ergebnissen führt. Es zeigte sich, dass die Anwendung der alternativen Vakuumschmelzmethode auf die Sauerstoffbestimmung in den untersuchten Proben Werte liefert, welche um 9-13% zu niedrig liegen.

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DETERMINATION OF ACTIVE TITANIUM IN TITANIUM POWDER USED IN PYROTECHNICS

by

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INTRODUCTION

When titanium powder is intended for use in pyrotechnics, it is important to know its active titanium (free titanium) and total titanium content.

Total titanium is usually determined by passing a solution of the sample through a Jones reductor and titrating with permanganate or ferric ammonium sulfate[1]. The total titanium can also be determined colorimetrically with hydrogen peroxide, using the differential colorimetry technique[2]. Another method for determining total titanium is to ignite the sample in air or oxygen and weigh the titanium dioxide produced[3,4].

The only method that has hitherto been used for the determination of active titanium is an indirect one in which the total of impurities and titanium compounds (titanium dioxide, titanium carbide and titanium nitride) are deducted from the sample weight. In titanium powder used for pyrotechnics the oxygen is present as titanium dioxide, rather than as a TiO phase as in commercial titanium. The following calculations have been used for a rapid approximation of the active titanium content of titanium powder containing only oxygen as a significant impurity:

$$\begin{aligned} \text{Let } X &= \%\text{ free titanium} \\ Y &= \%\ \mathrm{TiO_2} \\ Z &= \%\text{ total titanium} \end{aligned}$$

$$X + Y = 100, \text{ or } Y = 100 - X \quad \ldots\ldots\ldots\ldots \quad (1)$$

$$X + 0.5995\,Y = Z \quad \ldots\ldots\ldots\ldots \quad (2)$$

Substituting in equation (2) the value of Y as obtained in equation (1) and solving for X:

$$X = 2.497\,Z - 149.7$$

The above indirect method for determining active titanium has obvious disadvantages. In view of this, an investigation was undertaken to develop a direct method. As a first step in this investigation a survey was made of the methods that have been used in the determination of active metal in other metal powders.

METHODS FOR DETERMINING ACTIVE METAL IN METAL POWDERS

The following methods have been used for determining the active metal content of metal powders:

(1) Reaction of the metal with an acidic solution of a ferric salt or potassium dichromate, and titration of the ferrous ion or chromic ion produced. This method is not applicable to titanium because the titanous ion would interfere.

(2) Reaction of the metal with a neutral solution of an easily reducible salt such as mercuric chloride, ferric sulfate or silver nitrate, followed by filtration and determination of the amount of the metal found in the filtrate. This method is not applicable to titanium because titanium is passive in neutral solution.

(3) The use of a solvent that will separate the metal from the oxide. Differential solution methods are not applicable to titanium because no solvent is known that will separate metallic titanium from titanium oxide.

(4) Distillation of the metal in a vacuum, leaving the metal oxide behind. Such a method does not seem feasible for titanium because the boiling points of metallic titanium and titanium oxide are extremely high.

(5) Igniting the metal in hydrogen and weighing the reduced metal. This method is not applicable to titanium because titanium oxide is not reduced to the metal by hydrogen.

(6) Active aluminum has been determined by reacting the metal in a stream of dry hydrogen chloride gas at red heat, and then determining the aluminum chloride that distills over[5]. The metallic aluminum is attacked, and the aluminum oxide remains behind. The method seems applicable in principle to the determination of active titanium in a titanium powder that contains only oxygen as the significant impurity. If carbon or nitrogen are present in the sample, high results may be expected since the titanium carbide and titanium nitride would be attacked by the hydrogen chloride.

(7) Active aluminum has also been determined by reacting aluminum powder with litharge (PbO) at red heat and measuring the lead button produced[5]. Such a method might be applicable to titanium, because it also has a great affinity for oxygen.

(8) Reaction of the metal with acid or alkali and measurement of the hydrogen produced. The hydrogen can be oxidized with copper oxide and determined as water, or the hydrogen can be measured directly with a eudiometer. The hydrogen evolution reaction was found applicable to the determination of active titanium. Measurement of the hydrogen with a eudiometer was considered the most practical means of determining the hydrogen.

DETERMINATION OF ACTIVE TITANIUM BY THE EUDIOMETER METHOD

Fluoboric acid, or a mixture of fluoboric and sulfuric acids, was found to be the best medium for dissolving the sample. This mixture of acids was somewhat better than the fluoboric acid alone, because it dissolved the sample a little more readily. Other acids were not satisfactory. Sulfuric, hydrochloric, and perchloric acids dissolved the sample very slowly. Nitric acid and alkalis were practically without action. Phosphoric acid caused the precipitation of insoluble titanium phosphate. Hydrofluoric acid dissolved the sample rapidly but attacked the glassware.

In the reaction of the sample with the mixture of fluoboric and sulfuric acids a trace of hydrogen sulfide was generated, probably through the reduction of some sulfuric acid by titanium. The hydrogen sulfide does no harm since it is absorbed in the escarite contained in the U-tube that links the reaction flask to the gas buret of the eudiometer.

Other metals, if present in the titanium powder, will generate hydrogen if these metals are above hydrogen in the electromotive series. The amount of other metals found in titanium powder, however, will not produce errors greater than the experimental error of the method. The maximum amount of iron permissible in titanium powder is 0.15%, according to government specification.

Oxygen is the predominant impurity in titanium powder, the amount of carbon, nitrogen, and hydrogen being quite small. There is no danger that the carbon in titanium will form methane as is the case with beryllium. Titanium nitride in the metal reacts to form ammonium and titanous ions. This is the basis for the accepted method of determining nitrogen in titanium[6]. Consideration was given to the possibility that the oxygen present in the reaction flask might react with the titanous ion and thus produce an error in the measurement of the final volume of gas. It was found that no error was caused by this oxygen, since it was rapidly swept out of the reaction flask by the hydrogen. On cooling, some of the oxygen may diffuse, through the ascarite and the small openings in the stopcocks, back into the reaction flask. However, the final concentration of oxygen in the reaction flask would be too small to cause a significant error.

When titanium metal is dissolved in non-oxidizing acids, such as the fluoboric-sulfuric acid mixture, the titanous ion is formed because nascent hydrogen is generated. However, on standing, the titanous ion is oxidized slightly as shown by the following equation[7]:

$$Ti^{+3} + H^{+} \rightarrow Ti^{+4} + 0.5\ H_2$$

It is not believed that the hydrogen produced in the above reaction causes any significant error at the dilute acidity used in the proposed method. However, it should be emphasized that the determination of active titanium (like the determination of active metals in general) is somewhat empirical. That the results obtained for active titanium by the proposed method are reasonably close to the theoretical values is indicated by the fact that the results are within 0.3% of those obtained by the difference method previously mentioned. Even if somewhat empirical, the figure for active titanium is a significant one for control purposes in the manufacture of titanium powder used in pyrotechnics.

Apparatus

The apparatus used by the authors is shown in Fig. 1. The apparatus is modified from previous eudiometers in that a 500 ml bottle is placed beneath the gas buret to act as a reservoir for the expanded volume of gas produced when the reaction flask is heated. The recommended eudiometer differs also from the standard eudiometers in the method for dropping in the sample. In the standard eudiometer a sample of the metal powder is placed in a wadded filter paper which is dropped into an adapter tube above the reaction flask. A glass rod, protruding from a sidearm and extending across the bore of the adapter, prevents the sample from falling into the reaction flask. The glass rod is attached to the sidearm by means of rubber tubing, which permits retraction of the rod and release of the sample while maintaining a hermetic seal.

Some difficulty was experienced with this means of admitting the sample, as leaks developed in the rubber tubing. In view of this difficulty an improved device was developed for controlling the admission of the sample. The device consisted of a steel rod, 4 mm in diameter and 6 cm in length, sealed in a pyrex tubing of slightly larger diameter. This glass-enclosed steel rod was housed in the sidearm of the adapter and sidearm sealed. Movement of steel rod, back and forth across the bore of the adapter, was effected by means of an Alnico magnet.

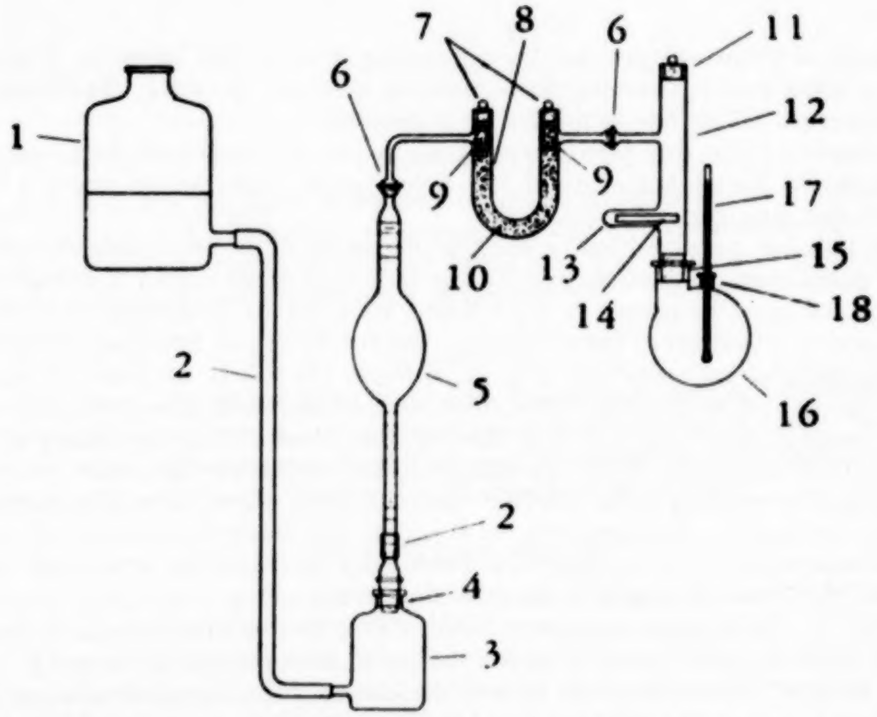

Fig. 1. Apparatus for the determination of active titanium in titanium powder.

1. Leveling bottle (capacity 1 liter)
2. Tygon or rubber tubing
3. Reservoir bottle (capacity 500 ml)
4. Ground glass joint (24/40) sealed with Dekhotinsky cement
5. Gas measuring buret (capacity 500 ml)
6. Ball joint
7. Ground glass joints (14/35) with stoppers
8. "U" tube, 15 mm in diameter
9. Glass wool
10. Ascarite
11. Ground glass joint (24/30) with stopper
12. Adapter, 25 mm in diameter and 17.5 cm long
13. Sidearm, 65 mm in length, 10 mm internal diameter
14. Iron bar sealed in a glass tube
15. Ground glass joint (29/42)
16. Reaction flask (capacity 250 ml)
17. Thermometer (0° to 100°C)
18. Ground glass joint (10/30)

All ground-glass joints and ball joints of the apparatus were held in place by springs or clips, and were ground together with carborundum paste. The liquid in the gas buret was 0.1% sulfuric acid solution colored with methyl red indicator and saturated with hydrogen gas. The solubility of hydrogen in this liquid is small but significant (1 ml of pure water at 25°C dissolves 0.017 ml of hydrogen when pressure of the gas over the water is 760 mm[8]).

References p. 233

Reagents

Acid mixture. Measure 280 ml of hydrofluoric acid (48 to 50 per cent) into a polyethylene beaker (conveniently made from a hydrofluoric acid container). Cool to below 5°C in an ice bath under the hood. Add 130 g of boric acid in small portions, while stirring with a plastic rod. Transfer the solution to a glass-stoppered bottle and add 700 ml of dilute sulfuric acid (5%). Saturate with hydrogen by passing hydrogen gas through the solution.

Dilute sulfuric acid (5%). Add 50 ml of sulfuric acid (sp. gr. 1.84) to about 800 ml of water. Cool to room temperature and dilute to 1 liter with water.

Dilute sulfuric acid (0.1%). Add 2 ml of sulfuric acid (sp. gr. 1.84) to 2 liters of water and add several drops of methyl red indicator solution. Saturate with hydrogen by passing hydrogen gas through the solution.

Procedure

Dry several grams of titanium powder by spreading it in a thin layer on a watch glass. Store this overnight in a dessicator containing fresh sulfuric acid (sp. gr. 1.84). The water content of the powder may be determined at the same time, if desired.

Weigh out a sample of the dry powder on a 9-cm No. 2 Whatman filter paper that has been folded in fluted fashion. Twist the ends of the filter paper together to make a wrapped sample that can fall freely through the adapter.

The amount of powder required for a sample depends upon the amount of active titanium present. It can be calculated approximately by the fact that at standard conditions of temperature and pressure 0.001426 g of titanium is equivalent to 1 ml of hydrogen. At room temperature (25°C), when the active titanium content is 94%, about 615 mg of titanium powder are required.

Assemble the apparatus as shown in Fig. 1. Grease all joints to prevent leaks. Pour about 1500 ml of dilute sulfuric acid (0.1%) containing methyl red indicator into the reservoir system. Pour 75 ml of the reagent acid mixture into the reaction flask. Drop the wrapped sample into the adapter above the reaction flask. Note the temperature of the thermometer in the reaction flask and compare it with the reading from another thermometer placed about 100 cm from the apparatus. If necessary, adjust the temperature in the reaction flask to correspond with the external temperature. The temperature of the reaction flask may be raised by warming the flask with the hands and lowered by immersion in a beaker of cold water.

With the stopper of the adapter removed, adjust the level of the liquid in the leveling bottle to the same level as in the gas buret. The level should be near the zero mark on the gas buret. Gently put in the stopper of the adapter, adjust the levels of the liquids again, and make an initial reading. Once the stopper of the adapter has been put in place, care should be taken to prevent leaks in the apparatus. Place the leveling bottle on a ring stand.

Using an Alnico magnet, retract the steel rod into the sidearm of the adapter. This will permit the sample to drop into the reaction flask. Place an 800 ml beaker containing about 500 ml of hot tap water under the reaction flask, then heat the beaker with a Bunsen burner until the temperature of the solution in the reaction flask reaches 85°C (no higher). Turn off the burner, but allow the beaker of hot water to remain in place until the sample has dissolved (about 3 minutes). Shake the reaction flask occasionally. As the sample is dissolving, lower the leveling bottle so that the levels of the liquid in the leveling bottle and the gas buret remain the same. This is essential to prevent leaks. After the reaction is complete, remove the beaker of hot water and replace it with a beaker of cold water. As the volume of hydrogen contracts, raise the leveling bottle again to keep the levels of liquids the same. When the reaction flask has cooled to the initial temperature, allow the system to stand for a few minutes to insure equilibrium. Equalize the levels of the liquid once more and make a reading on the gas buret. Read the barometric pressure from an accurate mercurial barometer and make a correction for the differences in coefficients of expansion of the mercury and glass[9]. Calculate the per cent active titanium as follows:

$$\text{Per cent active titanium} = \frac{R\,\dfrac{P\text{-}Pw}{760} \times \dfrac{273}{(273 + T)} \times 0.001426 \times 100}{W}$$

or:

$$\text{Per cent active titanium} = \frac{0.051223\ (P\text{-}Pw)\ R}{W\ \ (273 + T)}$$

where:

R = Reading of gas buret in ml
P = Reading of barometer in mm of mercury
Pw = Vapor pressure of water at temperature T
T = Temperature of system at equilibrium in degrees C
W = Weight of sample in grams.

References p. 233

Table I shows the results obtained when typical sample of titanium powder was run 7 times.

TABLE I

RESULTS FOR ACTIVE TITANIUM IN A TYPICAL TITANIUM POWDER USED FOR PYROTECHNICS

Active titanium found *Per cent*	*Average* *Per cent*	*Standard deviation* *Per cent*
94.17	94.05	0.104
94.16		
94.13		
93.99		
94.04		
93.91		
93.96		

SUMMARY

Possible approaches to the problem of determining active titanium in titanium powder used for pyrotechnics are discussed. A method is proposed for the determination whereby the sample is dissolved in a mixture of fluoboric and sulfuric acids and the volume of hydrogen evolved in the reaction measured. An improved eudiometer is described.

RÉSUMÉ

Le problème du dosage du titane actif dans des poudres de titane utilisées en pyrotechnique est examiné. Une méthode est proposée; elle consiste à dissoudre l'échantillon de poudre à analyser dans un mélange d'acides fluoborique et sulfurique; le volume d'hydrogène formé dans cette réaction est mesuré. Un modèle perfectionné d'eudiomètre est décrit.

ZUSAMMENFASSUNG

Das Problem der Bestimmung des aktiven Titans in Titanpulvern, welche in der Pyrotechnik verwendet werden, wurde erörtert. Eine Methode wurde vorgeschlagen welche daraus besteht, dass die Probe in einer Mischung von Fluorbor- und Schwefelsäure gelöst und das durch die Reaktion entwickelte Wasserstoffvolumen gemessen wird. Ein verbessertes Eudiometer wird beschrieben.

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THE SENSITIVITY OF SOME CHROMATOGRAPHIC SPRAYS

by

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The sensitivity of a number of reagents used to spray chromatograms was studied to enable a more intelligent choice of reagent to be made. Samples of aqueous solutions of twenty salts of analytical grade containing 5.0, 0.5, 0.05, 0.005, 0.0005 g of "cation" per litre were prepared by diluting the solution having the highest concentration**. Samples of the solutions were spotted in the centre of an area 2×2 cm on No. 1 Whatman filter paper. Those to be sprayed with oxine or quercitrin were spotted on the paper which had been extracted previously with hydrochloric acid[1] to remove the minute traces of iron, magnesium, and calcium which would react with these reagents — particularly oxine — forming compounds which are fluorescent.

Since preliminary experiments showed that the size of the spot on the paper was essentially constant for a given volume of solution, a pipette which delivered a suitable volume of solution was constructed according to the design of BANISTER[2]. The pipette was made by sealing a capillary tube about 1 cm long and 0.4 mm in diameter to a tube having an outside diameter of 7 mm. The lower half of the capillary was ground until it was a truncated cone, with the opening of the capillary at the flattened apex. By thrusting the tip of the capillary just below the surface of the solution, the liquid just filled the capillary. It emptied when the tip touched the paper. The pipette, calibrated by weighing the mercury in the capillary, was found to have a volume of 0.00127 ml from the prepared standard solution, which thus gave samples containing 6.4, $6.4 \cdot 10^{-1}$, $6.4 \cdot 10^{-2}$, $6.4 \cdot 10^{-3}$, and $6.4 \cdot 10^{-4}$ γ respectively of the "cation" on the paper.

Samples of each of the 26 cations having the same concentration were spotted on the paper so that when it was cut into strips 2 cm wide and approximately 60 cm long, there was a sample of each ion on the strip. In general, a similar strip for each reagent was prepared using solutions having the four highest concentrations.

Note

A polythene squeeze bottle sprayer used for toilet water can be used instead of the more elaborate equipment requiring compressed air ordinarily found in the laboratory. In some localities, 4 or 6 oz polythene bottles and an attachment permitting their use as a sprayer for insecticides or garden sprays are available. While the droplets are somewhat larger than those usually obtained in the laboratory, the results are reasonably satisfactory.

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* On sabbatical leave at the University of Bristol from the University of Minnesota.

** Blood pipettes can be used to make 1:10 or 1:100 dilutions.

Each strip was sprayed with a reagent and, after drying, was exposed to the fumes of ammonia, unless otherwise stated in Table I. The strips prepared by using the solutions of different concentrations after having been sprayed with a given reagent, were assembled. The colour of each spot of a sprayed cation was compared with that of the blanks similarly obtained (1) by the action of ammonia on an unsprayed spot of the cation, (2) by the action of the spray and ammonia on the water spot. A fifth strip was spotted with solutions containing $6.4 \cdot 10^{-4}\gamma$ of the cations, which gave positive spots at the next higher concentration. The smallest sample of the ion which gave a colour or fluorescence attributable to the reaction of the ion with the reagent in the spray — usually after exposure to fumes of ammonia — is the sensitivity of the reagent under the conditions used. Since the colours or fluorescence were just discernible using a sample of $6.4 \cdot 10^{-4}\gamma$, no tests involving a smaller sample were carried out. The reagents used as sprays and the composition of the solutions are given in Table I.

TABLE I

REAGENTS USED AS SPRAYS

Alizarin. Saturated solution in ethanol.
Alizarin Red S. 0.1% w/v in water.
Aluminon. 0.1% w/v aluminon, 1% w/v ammonium acetate in water.
Diphenylcarbazide. 1% w/v in ethanol.
Diphenylcarbazone saturated solution in ethanol.
Dithizone. 0.05% w/v in carbon tetrachloride.
Dimethylaminobenzylidine rhodanine. 0.02% w/v in ethanol.
2-Nitroso-1-naphthol-4-sulphonic acid (2NIN4SA)[2]. 0.05 g in 75 ml ethanol and 25 ml water.
Oxine. 0.5 g in 60 ml ethanol and 40 ml water.
* Lead cobalt nitrite. Spray with 5% w/v cobalt nitrate, 5% w/v lead nitrate, and 2 drops concentrated hydrochloric acid in water. After drying, spray with saturated $NaNO_2$ solution, wash, and dry.
* Potassium ferricyanide. 0.4% w/v in water.
* Potassium ferrocyanide. 0.4% w/v in water.
Quercitrin[4]. 0.2% w/v in ethanol.
Quinalizarin[5]. 0.05 g in 75 ml ethanol and 25 ml water.
Rhodizonic acid[2]. 0.1% w/v sodium salt in water.
Rubeanic acid. 0.1 g in 50 ml ethanol and 50 ml water.
* Sodium thiosulphate — cupric acetate[2]. Saturated solution of sodium thiosulphate and 0.4 g cupric acetate hydrate in 48 ml H_2O + 2 ml glacial acetic acid. Spray with sodium thiosulphate, warm, wash to remove excess thiosulphate and spray with cupric acetate solution.
Violuric acid. 0.1% w/v in water.
* Zinc uranyl acetate. Saturated solution of the reagent in 2*N* acetic acid — filter before using.

* not exposed to fumes of ammonia.

TABLE II

COLOUR SCHEME BASED UPON A UNIVERSAL INDICATOR CHART

Colour	*Abbreviation*	*pH*	*Colour*	*Abbreviation*	*pH*
Red	r	4.0	Green	g	7.5
Pink	p	5.0	Blue green	bg	8.5
Peach	ph	5.5	Green blue	gb	9.0
Orange	o	6.0	Blue	b	9.5
Yellow	y	6.5	Violet	v	10.0
Yellow green	yg	7.0	Red violet	rv	11.0

TABLE III

MOST SENSITIVE TESTS FROM:

Ion	A) COLOUR OF THE SPOT Limit of identification*	Reagents used**	B) FLUORESCENCE IN U.V. Limit of identification*	Reagents used**
Ag	10^{-2}	Diphenylcarbazide (br); dithizone (ph) ($5 \cdot 10^{-3}\ \gamma$); rhodizonic acid (br) ($2 \cdot 10^{-2}\ \gamma$).	10^{-2}	Rhodanine (bl); oxine (br).
Hg(I)	10^{-2}	Alizarin (rv); dithizone (ph); diphenylcarbazone (v) ($10^{-2}\ \gamma$).	10^{-2}	Rhodanine (br).
Pb	10^{-3}	Diphenylcarbazide (p).	10^{-2}	Oxine (br).
Cu	10^{-3}	Diphenylcarbazide (rv); diphenylcarbazone (br) ($2 \cdot 10^{-3}\ \gamma$).	10^{-3}	Quercitrin (bl); rhodanine (bl).
Bi	10^{-2}	Alizarin (rv); alizarin Red S (ph); diphenylcarbazone (rv).	10^{-2}	Oxine (br).
Cd	10^{-3}	Diphenylcarbazone (rv).	10^{-3}	Oxine (y).
Hg(II)	10^{-2}	Dithizone (ph) ($2.5 \cdot 10^{-1}\ \gamma$); diphenylcarbazone (v) ($1 \cdot 10^{-1}\ \gamma$).	10^{-2}	Rhodanine (br).
As(V)	10^{0}	Alizarin (rv); sodium thiosulphate-cupric acetate (br).	10^{0}	Rhodanine (g).
As(III)	10^{-1}	Alizarin (rv); diphenylcarbazone (p).	10^{0}	Rhodanine (g).
Sb(III)	10^{-1}	Alizarin (ph); alizarin Red S (y); dithizone (p) ($1 \cdot 10^{-1}\ \gamma$); thiosulphate-cupric acetate (br); diphenylcarbazone (p); quercitrin (br); sodium thiosulphate-cupric acetate (br).	10^{-2}	Oxine (yg); quercitrin (br).
Sn(II)	10^{-3}	Diphenylcarbazide (rv).	10^{-3}	Oxine (yg).
Sn(IV)	10^{-3}	Diphenylcarbazide (rv).	10^{-3}	Oxine (yg).
Co	10^{-4}	Diphenylcarbazone (p).	10^{-3}	Oxine (br).
Ni	10^{-4}	Diphenylcarbazone (v).	10^{-2}	Oxine (br); quercitrin (br); rhodanine (br).
Fe(III)	10^{-3}	Alizarin (v); diphenylcarbazide (rbr); 2-nitroso-1-naphthol-4-sulphonic acid (g) ($1 \cdot 10^{-2}\ \gamma$).	10^{-3}	Oxine (br); quercitrin (bl); rhodanine (br).
Al	10^{-3}	Alizarin (p) ($1.5 \cdot 10^{-1}\ \gamma$); aluminon (p) ($1.6 \cdot 10^{-1}\ \gamma$); diphenylcarbazone (rv); quercitrin (y).	10^{-4}	Oxine (yg).
Cr	10^{-2}	Alizarin (rv); aluminon (p); quercitrin (y).	10^{-2}	Oxine (br); quercitrin (br); rhodanine (br).
Mn	10^{-3}	Diphenylcarbazide (rv).	10^{-3}	Quercitrin (bl).
Zn	10^{-3}	Diphenylcarbazide (rv); diphenylcarbazone (p); dithizone (p) ($2.5 \cdot 10^{-2}\ \gamma$).	10^{-4}	Oxine (y).
Ba	10^{-2}	Rhodizonic acid (ph) ($2.5 \cdot 10^{-2}\ \gamma$).	10^{-3}	Oxine (y).
Sr	10^{-2}	Rhodizonic acid (ph) ($4.5 \cdot 10^{-1}\ \gamma$).	10^{-3}	Oxine (y).
Ca	10^{-1}	Alizarin (rv); diphenylcarbazide (p).	10^{-4}	Oxine (y).
Mg	10^{-2}	Alizarin (rv).	10^{-4}	Oxine (yg).
Na	—		10^{-2}	Zinc uranyl acetate (g) ($2.5\ \gamma$).
K	10^{0}	Lead cobalt nitrite (gr).	10^{0}	Quercitrin (y).
NH_4	10^{0}	Alizarin (y); lead cobalt nitrite (gr); quinalizarin (y).	10^{-1}	Rhodanine (o).

* In each case the exponential quantity should be multiplied by $6.4\ \gamma$.

** The abbreviations for colours are contained in Table II. The figures in brackets are the sensitivity of the reagent used as a spot test after the manner of FEIGL[3].

Note: In addition to the reagents mentioned above, the following reagents were tested: potassium ferricyanide, quinalizarin, rubeanic acid, and violuric acid. Under the conditions of our tests, these, though sensitive, were not the most sensitive for the particular ion.

It was found difficult to describe the colours of the sprayed spots. Finally the chart supplied by the British Drug Houses for use with their Universal Indicator was used as a reference. The names assigned to and abbreviations used for the colours corresponding to the various pHs are given in Table II.

By using these reference colours together with brown (br), grey (gr), and black (bl), it was possible to indicate the colours of the spots reasonably well. However, the illumination, colour perception of the observer, *etc.* undoubtedly influence the description of the colour.

In Table III, subject to the colour sensitiveness, *etc.* of the observer's eyes, the most sensitive reagents for the ions are tabulated. In columns 2 and 4, the limits of identification are given for the cations when sprayed with the reagents listed in columns 3 and 5 respectively. Where available, the sensitivity of the reagent is quoted, in brackets, for its use as a spot test after the manner of FEIGL[3]. In general, the quantity of an ion which can be detected when the reagent is used as a spray is equal to or somewhat less than that when the reagent is used to spot the ion.

SUMMARY

The limits of identification of twenty six common cations, with a selected number of spray reagents used in paper chromatography, have been determined. A table of the most sensitive tests is given.

RÉSUMÉ

On a déterminé les limites d'identification de vingt-six cations courants, avec une série de réactifs de développement utilisés en chromatographie sur papier. Un tableau des réactions les plus sensibles est donné.

ZUSAMMENFASSUNG

Die Identifizierungsgrenzen von sechsundzwanzig gewöhnlichen Kationen mit einer Reihe von ausgewählten Entwicklungsreagenzien, die in der Papierchromatographie benützt werden, wurden ermittelt. Die Arbeit enthält eine Tabelle der empfindlichsten Reaktionen.

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THE EMPLOYMENT OF A R.Rf. TITRIMETER IN CONJUNCTION WITH BLAKE'S R.Rf. CHROMATOGRAPH ZONE LOCALIZER

by

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Since the writer published his paper on the location and quantitative evaluation of visible and invisible chromatographic zones by his R.Rf. impedance method[1], he has incorporated a conductimetric tube with the zone localizer. This, when connected to the rectifying circuits of the latter, acts as a titrimeter and enables quantitative evaluations to be carried out in less time than is possible by the planimetric method of area measurement.

Before describing the apparatus, brief reference to some of his early work on the conductivity of dilute solutions is revelant. The following quotations indicate the capabilities of the R.Rf. methods in regard to the detection and measurement of extremely small quantities of a solute when in aqueous solution.

In 1945, BLAKE[2] described his Q-metric circuit for the automatic control of solution concentration, and later, in 1947[3], with a more sensitive arrangement, succeeded in operating his circuit either by addition or alternatively by the subtraction of only one ml of a saturated solution of thiosulphate in 60 l of water. This circuit was suggested for the automatic control of thiosulphate elimination when washing photographs[4].

Q-metric measurements

In 1949[5], still employing his Q-metric circuit, he showed that, when the anode current variations caused by changes in solution concentration were plotted against a series of dilutions of HCl covering a range between $0.00025M$ and $0.01M$, the resultant curve was parabolic.

R.Rf. measurements

In 1950, BLAKE[6] covered the range between $0.000012M$ and $0.1M$ with his R.Rf. titrimeter and showed again that the curve was parabolic. Each concentration plotted throughout this series was half as concentrated as its predecessor. In practice, when making quantitative measurements, the concentrations are usually fairly close to each other, and the portion of the curve covered is so short that it is not distinguishable from a linear graph.

Zone location

When employing the writer's early type of zone localizer[7], it was necessary to spray the chromatographs with water to increase their conductivity before passing them across the electrodes of the localizer.

The introduction of "doubled electrodes"[8] enabled the zones to be located at ambient humidity. Even the very weakest zones could be located after enclosing them for a short time in a humidor, or exposing them to steam.

Following this, the writer[9] more than doubled the sensitivity of the instrument by the employment of a new circuit which combined full-wave rectification with negative zero set-back. A number of chromatographs were reproduced and quantitative measurements were made by area measurement similar to those obtained when this work is carried out photometrically. At this stage J. C. McPhillips and N. S. Snow (who are using the writer's method of zone localization at the Department of Agriculture at Sydney University) suggested that the writer's R.Rf. titrimeter[6] might be employed for quantitative measurement of the solutes contained in the chromatograph zones. The writer tested this suggestion and, as it proved very successful, he has incorporated a conductimetric tube with his zone localizer.

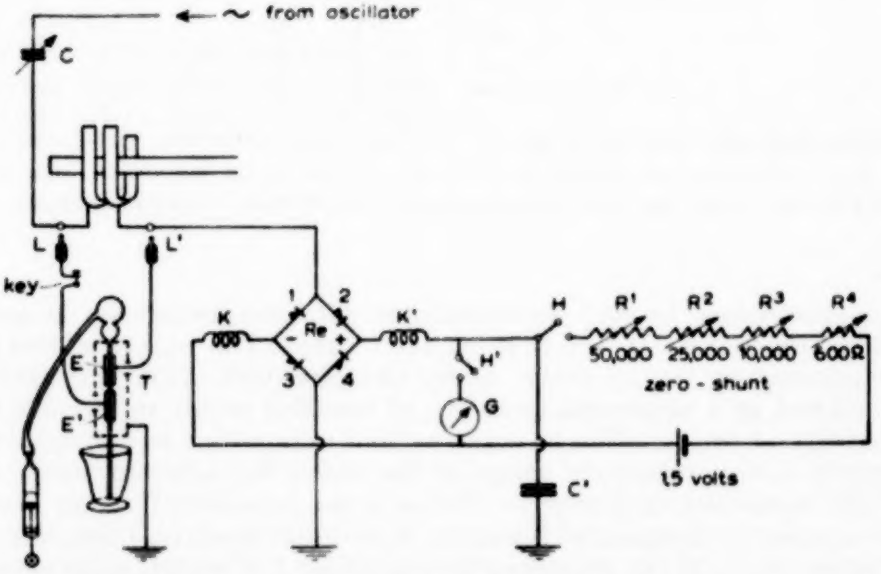

Fig. 1. This diagram illustrates the addition of a conductimetric tube to Blake's R.Rf. chromatograph zone localizer.

The circuits are so arranged (Fig. 1) that only one set of controls is required and this operates either the zone localizer or the titrimeter. The writer obtains his Rf. current from a Hartley-Child oscillator operating at 1000 Kcs. The frequency as long as it be stable is not at all critical, and any stable type of oscillator could be employed.

The output from the oscillator is fed through a small variable coupling condenser *C* (having a maximum capacitance of about 5 Pf). The zero-shunt and also the four crystal rectifiers marked *Re 1-4* are arranged to give full-wave rectification[8,9]. They not only serve the localizer, but also the conductimetric tube *T*, where they take the place of the usual single crystal rectifier employed for titration and concentration measurement. This circuit is twice as sensitive.

The conductimetric tube *T* is connected across the "doubled electrodes" *E* and *E'* of the localizer. It is plugged in when required at *L* and *L'*. In the absence of a chromatograph, the capacitance between the electrodes is negligible and there is no need for them to be disconnected from the oscillator while the titrimeter is in use. The rest of the circuit is the same as that previously described[8]. Details of the conductimetric tube are well known[5,6]. The only difference in this case is that the dimensions are considerably reduced (Fig. 2).

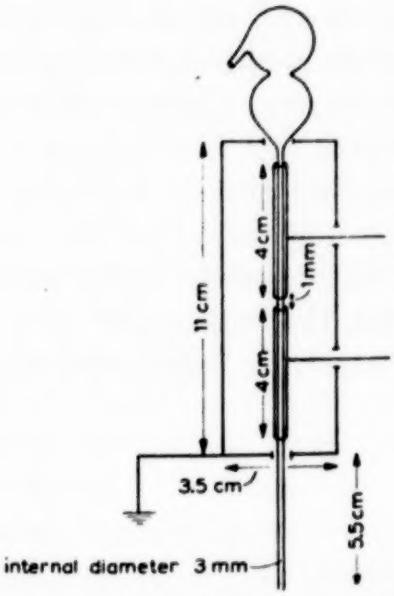

Fig. 2. This diagram provides the dimensions of the conductimetric tube which, when used in conjunction with the full-wave rectification circuit of the zone localizer, operates as a micro-titrimeter also for the comparison of solution concentrations.

Mode of operation

After formation (sometimes termed development) the chromatograph is passed across the electrodes of the localizer and the zones or spots are located. The nature of the solute contained in each zone is determined by its R_F value, or by chemical test. After this each zone is cut out with scissors and soaked in a measured quantity of distilled water to extract the solute. 2 ml is a convenient quantity of this solution to make up and with which to commence measurements. If the meter deflection is not within the range of the meter the solution must be diluted by the addition of a further measured quantity to obtain some convenient meter reading *X*.

The next step is to make up a measured quantity of a similar stock solution, say 1 l, by dissolving a quantity of the same chemical (in measured amounts)in 1 l of water, until after repeated titrimeter tests this new solution gives the same meter deflection *X*. Both solutions now contain an equal amount of the solute per unit quantity of the solution. The strength of the solution is known from the quantity of solute in the stock solution.

The process of solution matching could of course be modified by adding small quantities of distilled water to a known amount of solute until the required reading is obtained.

One of the advantages of this new method is that by dissolving the content of each zone in water, maximum conductivity is assured; in addition to this the difficulties due to variations in ambient humidity are entirely obviated.

SUMMARY

This paper describes a new departure in quantitative paper chromatography. A conductimetric tube has been incorporated with BLAKE's R.Rf. zone localizer.

The advantages of this new method are:

1. The meter deflections are unaffected by changes in atmospheric humidity.
2. When in aqueous solution, the solute exhibits its maximum conductance and therefore gives much larger meter deflections.
3. This method provides a considerable saving of time.

References p. 241

RÉSUMÉ

Une nouvelle technique de chromatographie quantitative sur papier est décrite. Un tube conductimétrique est incorporé à l'appareil de localisation des zones de BLAKE.

Cette méthode présente les avantages suivants:

1. Les mesures ne sont pas influencées par les variations de l'humidité atmosphérique.
2. En solution aqueuse, la conductance est maximum et on observe de beaucoup plus fortes déviations.
3. Cette méthode permet de réaliser un gain de temps considérable.

ZUSAMMENFASSUNG

Ein neues Verfahren für die quantitative Papierchromatographie wird beschrieben. Hierbei wird ein konduktimetrisches Rohr in den Zonenlokalisierungsapparat von BLAKE eingeschaltet.

Die neue Methode bietet folgende Vorteile:

1. Die Meterausschläge werden von Änderungen der atmosphärischen Feuchtigkeit nicht beeinflusst.
2. In wässriger Lösung ist die Leitfähigkeit maximal, sodass man viel grössere Ausschläge erhält.
3. Die Methode ermöglicht eine bedeutende Zeitersparnis.

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HYDRAZINOPHTHALAZINES

I. ORGANIC REAGENTS FOR THE DETERMINATION OF IRON

by

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With the aim of modifying, as far as possible, the pharmacological and clinical properties of hydrazinophthalazines, we studied some of their derivatives. In the course of this work we noticed that these compounds give typical colorations with metallic ions, and in particular with ferric iron.

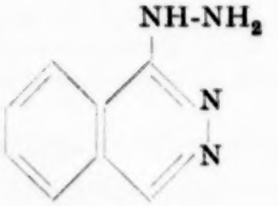
The exceptional sensitivity of these phthalazines towards the ferric ion and the possible analytical applications of these substances indicated that the reactions should be placed on record.

EXPERIMENTAL

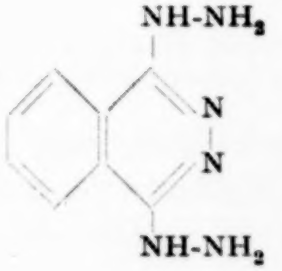
Reagents employed

Hydrochloric acid dil.
Ammonium hydroxide dil.
Sodium acetate 10%, pH 9
Sodium citrate 10%, pH 8.5
Sodium tartrate monobasic 5%, pH 2.5
Sodium phosphate monobasic 10%, pH 3.5
Sodium phosphate dibasic 10%, pH 10.5
Sodium oxalate 4%, pH 7.8

The structures of the reagent, hydrazinophthalazine(I), and dihydrazinophthalazine(II), are as follows:



(I)



(II)

Sensitivity to Fe^{+3}

Very dilute solutions of Fe^{+3} and (I) give a violet colour with a blue tint, while (II) yields a violet colour with a red tint. The sensitivity towards Fe^{+3} is greater for (II) than for (I), but the instability of the colour produced with (II) makes the reagent unfit for colorimetric or spectrophotometric use. (II) detects very small amounts (0.002 γ/ml of Fe^{+3}) rapidly, whereas (I) detects rather larger amounts.

Strong mineral acid prevents the formation of the above-mentioned colours, but once these colours are formed, strong mineral acid only diminishes the colours. After some time the colour becomes stronger and the two shades of violet assume the same tone; after twelve hours, colorimetric observations can be made with the naked eye for even smaller amounts of iron.

Spectrophotometry

Hydrazinophthalazine(I)

When solutions containing 60 to 100 γ/ml of $FeCl_3 \cdot 6\ H_2O$ in the presence of an excess of reagent (I) (0.10 g/100 ml solution) were examined by the Beckman spectrophotometer (model D.U. with Corex cells) a good maximum absorbancy was observed only after twelve hours. *Spectrophotometric characteristics:* minimum absorbancy 458 mμ, maximum absorbancy 565 mμ, specific absorbancy small, not sufficient for determinations.

Dihydrazinophthalazine(II)

Solutions from 20 to 40 γ/ml were examined as above; a greater specific sensitivity was found and, at the same time, a relatively greater specific absorbancy was observed. *Spectrophotometric characteristics:* minimum absorbancy 460 mμ, maximum absorbancy 546 mμ, specific absorbancy relatively greater.

Buffers

The reading of the colorimeter should be made 20-30 minutes after the start of the reaction. In the range 20—100 γ/ml of iron, good agreement with Beer's law was obtained, with a greater sensitivity for (II). However, the poor stability of the colours prevented us from making full use of the specific sensitivity of these reagents to ferric ion in colorimetric determinations. It seemed as if it might be possible to stabilize the colours by using buffer solutions, and many were tried with various results, as shown in Table I.

TABLE I

Buffer used	*Hydrazinophthalazine (I)*	*Dihydrazinophthalazine (II)*
Sodium acetate 10%, pH 9	Sensitivity greatly increased, tint turned to red, stability increased	Sensitivity greatly increased, tint turned to blue, stability almost equal to (I)
Sodium citrate 10%, pH 8.5	As above, but to a lesser degree	As above but to a lesser degree
Sodium phosphate monobasic 10%, pH 3.5	Decoloration	Decoloration
Sodium phosphate dibasic 10%, pH 10.5	Sensitivity and stability somewhat improved	As for sodium citrate
Sodium oxalate 4%, pH 7.8	Decoloration	Decoloration
Sodium tartrate monobasic 5%, pH 2.5	Sensitivity not improved	Sensitivity not improved

Conclusions. The best buffers as regards sensitivity and stability were found to be sodium acetate and sodium citrate; both stabilize the colour, but produce a red tint, except in the case of (II), which turns blue 10—15 minutes later.

Spectrophotometric measurements

For this purpose the sodium acetate buffer was also found to be the most useful and the most stable buffer for colorimetric or spectrophotometric measurement.

Dihydrazinophthalazine with a sodium acetate buffer is highly sensitive (specific absorbancy about 1250), but its colour rapidly fades; hydrazinophthalazine undoubtedly is the best for stability of colour and for specific sensitivity; good readings were obtained up to 30 minutes after the reaction, although the best were those made after an interval of 15—20 minutes; during this period Beer's law is obeyed. By varying the pH of the buffer, the best results were obtained using a solution of 10% sodium acetate of pH 11.2—11.3.

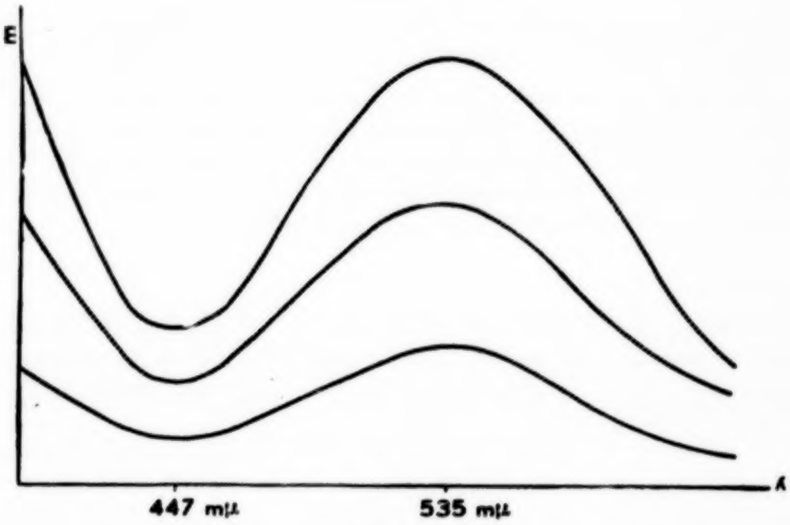


Fig. 1.

Amounts of from 3—13 γ/ml were used, the solution was buffered with 10 ml of 10% sodium acetate, pH 11.2, 0.05 g of (I) added and the whole diluted to 100 ml with water. This was read against a reagent blank, after an interval of 15—30 minutes. Good agreement with Beer's law was observed and a reference curve was rarely needed.

Spectrophotometric characteristics: minimum absorbancy 447 mμ, maximum absorbancy 535 mμ, $E^{1\,\%}_{1\,\mathrm{cm}} = 1233$ for Fe^{+3}.

Very good readings were obtained with a colorimeter, using appropriate filters.

TABLE II

INTERFERENCES FOR SOLUTIONS CONTAINING 100 γ/ml OF $FeCl_3 \cdot 6\ H_2O$

Element	*Salt used*	*Minimum amount that interferes (γ)*	*Indication of interference*
Co	$Co(NO_3)_2 \cdot 6\ H_2O$	0.01	+
Ni	$NiSO_4 \cdot 6\ H_2O$	0.001	—
Cr	$CrK(SO_4)_2 \cdot 12\ H_2O$	0.005	—
Mo	$(NH_4)_6Mo_7O_{24} \cdot 4\ H_2O$	0.01	—
W	$Na_2WO_4 \cdot 2\ H_2O$	0.4	—
Mn	$MnCl_2 \cdot 4\ H_2O$	0.4	—

All oxidizing ions (MnO_4^-, CrO_4^{-2}, $Cr_2O_7^{-2}$, NO_2^-, NO_3^-, Ce^{+4}, *etc.*), as well as oxalate and phosphate, interfere.

The analytical characteristics of (I) are compared in Table III with those of a few common reagents for the colorimetric determination of iron as ferric ion.

TABLE III

Reagent	*Sensitivity Fe^{+3} γ/ml*	*Stability of colour*	*Acidity and pH range*	*Effect of excess of reagent*	*Beer's law*
Thiocyanate	0.008 (480 mμ)	Fades rapidly unless stabilized	0.05-1*N*	Increases intensity	Slight deviation
Thiocyanate and acetone	0.004 (480 mμ)	Fades	0.05-1*N*	Increases intensity	Slight deviation
Mercaptoacetic acid	0.014 (540 mμ)	Lasts for several hours	7-12	None	Obeyed
Hydrazinophthalazine(I)	0.002 (535 mμ)	Lasts for several hours when stabilized	10-12	None	Obeyed

This table is partly based on data given by WOODS AND MELLON*.

Compared with the thiocyanate method, the described method has the advantage of not being influenced by the quantity of reagent, which is already in excess in the present method. The thiocyanate-acetone method makes extractions necessary, and these are always troublesome; the mercaptoacetic acid method always gives the ferric iron together with the ferrous iron.

SUMMARY

Two new organic reagents for the determination of ferric iron, hydrazinophthalazine and dihydrazinophthalazine, are proposed .They yield a red-violet colour which is stabilized with 10% sodium acetate at pH 11.2. Good results are obtainable in colorimetric and spectrophotometric determinations, especially with hydrazinophthalazine, Beer's law being obeyed. Interferences with other ions or metals are recorded and the advantages of these reagents over others are pointed out.

RÉSUMÉ

Deux nouveaux réactifs sont proposés pour le fer(III): l'hydrazinophtalazine et la dihydrazinophtalazine. On obtient alors une coloration rouge-violet, stabilisée en solution tamponnée à l'acétate de sodium (pH 11.2). On peut effectuer des dosages colorimétriques et spectrophotométriques. La loi de Beer est obéie, principalement avec l'hydrazinophtalazine. L'auteur a étudié l'influence d'autres ions et il décrit les avantages de ces deux réactifs.

ZUSAMMENFASSUNG

Zwei neue organische Reagenzien für Ferriionen, Hydrazinophtalazin und Dihydrazinophtalazin wurden vorgeschlagen. Sie geben eine rotviolette Färbung, die mit 10%igem Natriumacetat, bei pH 11.2 stabilisiert wird. Gute kolorimetrische und spektrophotometrische Bestimmungen sind möglich, da das Beersche Gesetz genau befolgt wird, besonders mit Hydrazinophtalazin. Die störenden Einflüsse anderer Metalle oder Ionen wurden untersucht. Die Vorteile der beiden neuen Reagenzien gegenüber anderen wurden hervorgehoben.

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* J. T. WOODS AND M. G. MELLON, *Ind. Eng. Chem., Anal. Ed.*, 13 (1941) 554.

HYDRAZINOPHTHALAZINES

II. ORGANIC REAGENTS FOR THE DETERMINATION OF VANADIUM

by

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During the study of the behaviour of the hydrazinophthalazines as organic reagents, a high sensitivity towards vanadium salts was observed.

These reagents, already used for the determination of iron[1], have proved satisfactory for the determination of vanadium on account of their high sensitivity, especially in colorimetric or spectrophotometric measurements.

EXPERIMENTAL

Reagents employed. They were the same as described in the previous communication[1].

Sensitivity to vanadium

On adding small amounts of hydrazinophthalazine (I) or dihydrazinophthalazine (II) to very dilute solutions of NH_4VO_3 (1 γ/ml), a straw-yellow colour is quickly obtained; for solutions containing 0.01 γ/ml about 10 to 15 minutes are necessary for development of colour. When the concentration is increased, the colour deepens, and on a further increase a precipitate is obtained.

As in the case of iron[1], (II) is more sensitive than (I), but its colour fades rapidly. Therefore, for present purposes, (II) was abandoned and improvements were made in the sensitivity and the stability of colour obtained with (I) (see Table I).

TABLE I

Reagent used	*Variation of colour noted*
Hydrochloric acid dil.	Colour diminishes
Ammonium hydroxide dil.	Colour hardly appears
Sodium acetate 5%, pH 9	Brown tinge intensifies
Sodium citrate 10%, pH 8.5	Like sodium acetate, but less definite
Sodium tartrate monobasic 5%, pH 2.5	Loses colour after one hour
Sodium phosphate monobasic 10%, pH 3.5	Like sodium acetate
Sodium phosphate dibasic 10%, pH 10.5	Like sodium acetate
Sodium oxalate 4%, pH 7.8	Like sodium acetate (different from iron)

The 5% sodium acetate proved most efficient.

Spectrophotometry

On measuring the absorbancies of NH_4VO_3 solutions and (I), a fairly stable maximum was found at 440 mμ, but Beer's law was not obeyed. This maximum is thus not fit for quantitative analysis as it is too weak. However, fair comparisons are still possible with the naked eye, with good approximation; the above also applies to (II).

Buffered solutions were used for increasing the stability of the colour and a 5% solution of sodium acetate was chosen, with a pH at which Beer's law was best obeyed; in this case it was found to be in the zone near to neutrality, *i.e.*, at pH 5.5. Buffered sodium acetate solutions were adjusted by adding sodium hydroxide or acetic acid as needed.

Thus, good agreement with Beer's law was found, the maximum absorbancy being at 442 mμ; specific absorbancy varies slightly with the concentration.

$$\text{From } 0.5 \text{ to } 2\ \gamma/\text{ml of V, } E^{1\%}_{1\,\text{cm}} = 1380$$

$$\text{From } 2 \text{ to } 4\ \gamma/\text{ml of V, } E^{1\%}_{1\,\text{cm}} = 1400$$

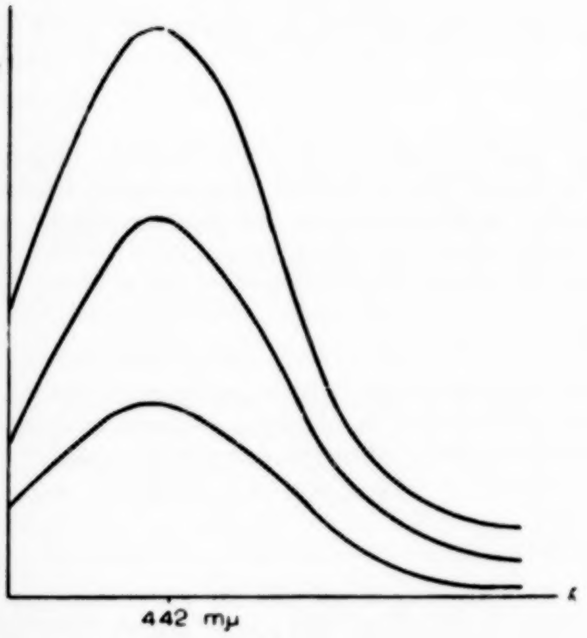

Fig. 1.

The best readings were those taken 5-10 minutes after the start of the reaction, against a reagent blank. For each reading 0.02 g of (I) and 10 ml of 5% sodium acetate pH = 5.5 were taken and diluted to 100 ml.

Good results were also obtained on working with a colorimeter under analogous conditions, but using solutions of from 10 to 50 γ V/ml.

Interferences

TABLE II

INTERFERENCES FOR SOLUTIONS CONTAINING 100 γ/ml OF NH_4VO_3

Element	*Salt used*	*Minimum amount that interferes (γ)*	*Indication of interference*
Fe	$FeCl_3 \cdot 6\,H_2O$	0.01	+
Co	$Co(NO_3)_2 \cdot 6\,H_2O$	0.015	+
Ni	$NiSO_4 \cdot 6\,H_2O$	0.015	—
Cr	$CrK(SO_4)_2 \cdot 12\,H_2O$	0.015	+
Mo	$(NH_4)_6Mo_7O_{24} \cdot 4\,H_2O$	0.005	+
W	$Na_2WO_4 \cdot 2\,H_2O$	0.001	—
Mn	$MnCl_2 \cdot 4\,H_2O$	0.005	—

All oxidizing agents (MnO_4^-, CrO_4^{-2}, $Cr_2O_7^{-2}$, NO_2^-, NO_3^-, Ce^{+4}, *etc.*) interfere.

In Table III the analytical characteristics of (I) are compared with those of two of the commoner organic reagents used for the colorimetric determination of vanadium.

TABLE III

Reagent	*Sensitivity γ/ml*	*Stability of colour*	*Acidity and pH range*	*Effect of excess of reagent*	*Beer's law*
Phosphotungstate	0.03 (400 mμ)	Lasts for several hours	0.5*N*	None, if solution is boiled	Obeyed
Peroxide	0.02 (450 mμ)	Lasts for several hours	0.6-6*N*	Reduces intensity	Obeyed
Hydrazinophthalazine	0.02 (442 mμ)	Lasts for several hours	5-6	None	Obeyed

This table is partly based on data given by SANDELL[2].

The method using hydrazinophthalazine therefore offers the advantage of insensitivity to an excess of reagent (which is not the case with H_2O_2) and of not necessitating any special treatment, such as boiling the solution, which is necessary with the phosphotungstate method.

SUMMARY

Hydrazinophthalazine and dihydrazinophthalazine were found to be good organic reagents for the determination of vanadium. They develope a stable straw-yellow colour in 5% sodium acetate at pH 5.5. Colorimetric and spectrophotometric determinations are easily carried out. Beer's law is obeyed reasonably well. Interferences with other metals or ions are recorded and the advantages of the described method with reference to others commonly used are pointed out.

RÉSUMÉ

L'hydrazinophtalazine et la dihydrazinophtalazine réagissent avec le vanadium en donnant une coloration jaune paille stable, au pH 5.5. Ces réactifs permettent des dosages colorimétriques et spectrophotométriques. L'auteur a étudié également l'influence d'autres ions et il a décrit les avantages de cette méthode.

ZUSAMMENFASSUNG

Es wurde festgestellt, das Hydrazinophtalazin und Dihydrazinophtalazin gute organische Reagenzien für Vanadin sind; sie entwickeln eine strohgelbe Färbung, die mit 5%igem Natriumacetat bei pH 5.5 am besten stabilisiert wird. Kolorimetrische und spektrophotometrische Bestimmungen sind jederzeit möglich, da die Lösungen fast genau dem Beer'schen Gesetze folgen. Die störenden Einflüsse anderer Metalle oder Ionen wurden ermittelt. Es wurde auf die Vorteile der beschriebenen Methode gegenüber anderen sonst üblichen Methoden hingewiesen.

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NACHWEIS VON THALLIUM MIT METHYLVIOLETT

von

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Thallium und Antimon reagieren in ähnlicher Weise mit Rhodamin B, wobei ein violettgefärbter Niederschlag entsteht der durch Benzol extrahierbar ist.

V. I. Kuznecov[1] benutzt zum Nachweis von Antimon eine Farbreaktion mit Methylviolett. Bei dieser Reaktion, die in salzsaurer Lösung durchgeführt wird, ergibt sich ein Farbumschlag von gelb-grün nach blau. Auch diese farbige Verbindung wird durch Benzol extrahiert.

Die bessere Erhältlichkeit von Methylviolett und die oben erwähnte Ähnlichkeit der Reaktion von Thallium und Antimon veranlasste uns zu dem Versuch, dieses Reagenz zum Nachweis von Thallium zu verwenden.

Als Reagenz wurde eine 0.2%ige wässrige Lösung von Methylviolett verwendet. Ein positiver Verlauf der Reaktion ist nur in Gegenwart von Thallium(III)-Salzen möglich und deshalb ist es nötig, Thallium(I)-Salze zu oxydieren. Diese Oxydation wird mit Bromwasser durchgeführt und der Überschuss an Bromwasser durch Sulfosalicylsäure reduziert.

Zum Nachweis wurde die von F. Feigl[2] beschriebene Ausführung für den Nachweis von Thallium mit Rhodamin B benutzt.

Ausführung. Zu einem Tropfen der Probelösung in einem Mikroprobierrohr füge man einen Tropfen Bromwasser, einige Kristalle fester Sulfosalicylsäure, 2 Tropfen konzentrierter Salzsäure und 2 Tropfen von 0.2%iger wässriger Methylviolettlösung. Nach Zugabe von ca. 0.2 ml Benzol wird geschüttelt. Bei Anwesenheit von Thallium wird die Benzolphase blau gefärbt: pD = 6.

Eine positive Reaktion entsteht auch bei Gegenwart von Hg, Au, Sb und MoO_4^{-2}. Die Störungen von Hg, Au und Sb kann man durch Reduktion dieser Metalle durch metallisches Kupfer in saurer Lösung beseitigen. VO_3^- und WO_4^{-2} -Ionen verursachen auch eine blaue Färbung, die aber nicht in die Benzolphase übergeht.

ZUSAMMENFASSUNG

Thallium kann durch seine Farbreaktion mit Methylviolett nachgewiesen werden. Diese Reaktion ist sehr empfindlich und selektiv.

SUMMARY

Thallium can be identified by its colour reaction with methyl violet. This reaction is very sensitive and selective.

RÉSUMÉ

Le thallium peut être identifié par la réaction colorée, au moyen du violet de méthyle. Cette réaction est très sensible et sélective.

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Eingegangen den 7. November 1956

ANALYSIS OF THE TERPHENYLS BY A COMPRESSED PELLET INFRARED METHOD* INVOLVING MICRO-DISTILLATION

by

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Infrared spectrophotometry has been used by a few investigators for the identification of various polyphenyl compounds. The extensive spectra listings of both BARNES *et al.*[1] and CANNON AND SUTHERLAND[2] include infrared curves for biphenyl, *ortho-*, *meta-*, and *para*-terphenyl and several higher polyphenyls. These data indicate the possibility of developing quantitative methods of analysis by utilizing infrared absorption in the region 5-15 microns. Quantitative infrared spectrophotometry on the terphenyls has been under development in this laboratory as a method of evaluating irradiation damage. Solution (carbon tetrachloride and carbon disulfide), mull (Nujol and chlorinated hydrocarbons[3]) and compressed pellet methods have been tried.

Mull techniques proved unsatisfactory here due to interference from the spectrum of the mull liquids. In addition to Nujol, experiments were performed using the mull solvents, hexachlorobutadiene and tetrachloroethylene, recommended by ARD[3]. Even in an infrared spectral region of solvent transparency, quantitative accuracy was poor in using any of the mull solvents. These results were not reproducible presumably due to an inability to maintain uniform dispersion and sample thickness.

Polyphenyls, higher than the terphenyls, possess only a very limited solubility in solvents (carbon tetrachloride and carbon disulfide) commonly used in infrared analysis. The compressed pellet technique eliminates this solubility difficulty and is potentially applicable for infrared determinations on all polyphenyl compounds. The method has been developed at present for the quantitative analysis of the terphenyls in radiation damaged samples.

EXPERIMENTAL

Apparatus

Infrared spectra were measured over the range 2-15 microns with a Perkin Elmer, Model 21, double beam, infrared spectrophotometer. A sodium chloride prism was employed. A stainless steel pellet holder was constructed, rectangular in shape, with a raised platform on which the solid pellet rests. The holder had a 0.490 inch diameter hole in the center around which was a 0.005 inch lip for positioning the pellet. The pellet was secured in place by a plate which also had a 0.49 diameter hole with a 0.045 inch lip. The plate was centered and held in place by three screws. The lip served to screen out edge effects on the solid pellets.

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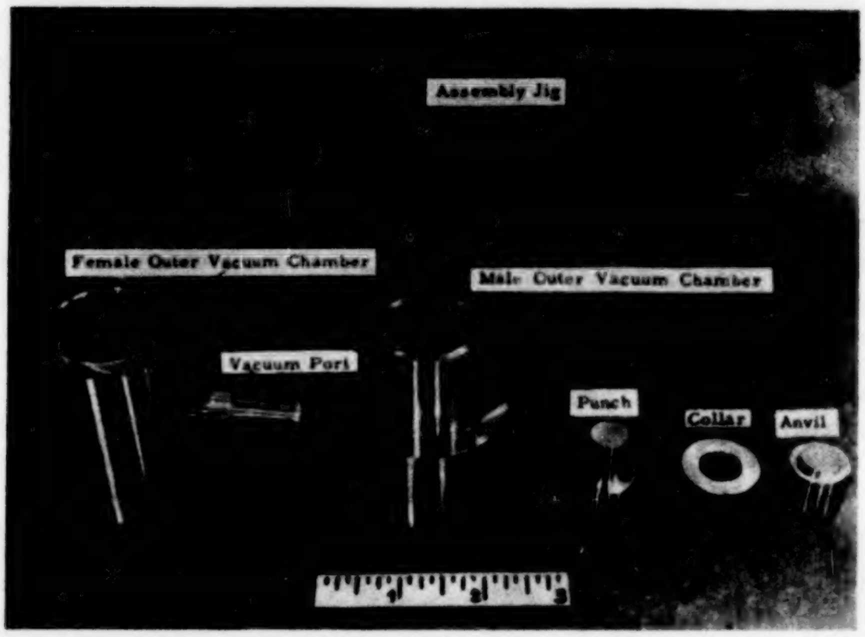
Assembly Jig
Female Outer Vacuum Chamber
Male Outer Vacuum Chamber
Vacuum Port
Punch
Collar
Anvil
1
2
3

Fig. 1A. Vacuum die assembly. Pictorial view.

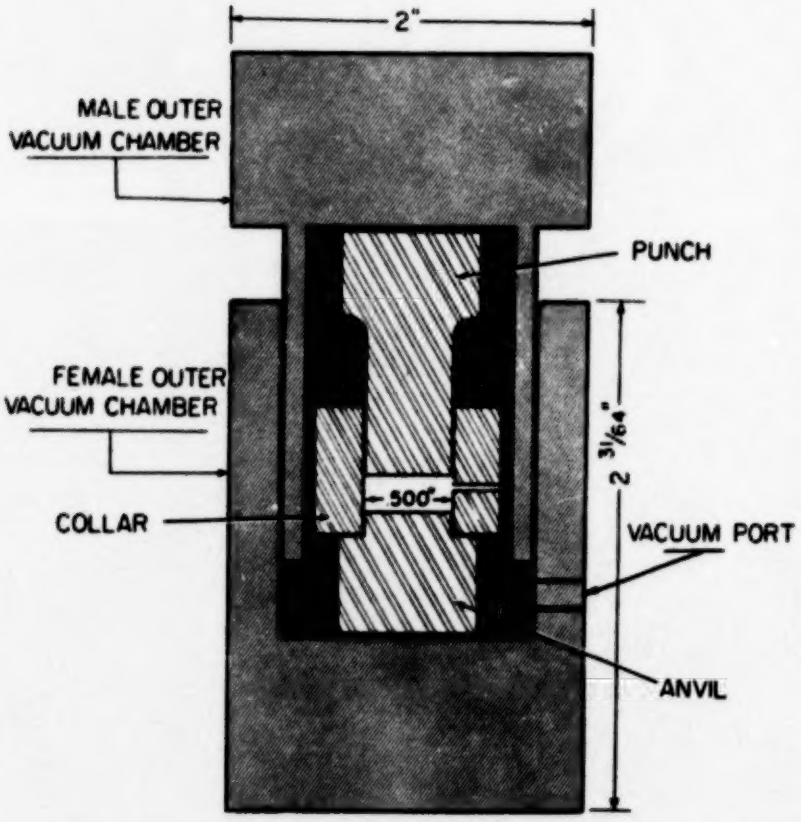
2"
MALE OUTER VACUUM CHAMBER
PUNCH
FEMALE OUTER VACUUM CHAMBER
2 31/64"
.500"
COLLAR
VACUUM PORT
ANVIL

Fig. 1B. Vacuum die assembly. Schematic diagram.

The vacuum die assembly (Fig. 1a) consists of the die and an outer vacuum chamber. The die itself contains three pieces, an anvil, a collar and a punch. The collar has a small hole which allows the material inside to be evacuated while being pressed. The outer vacuum chamber consists of two close fitting concentric cylinders with a vacuum port. The die assembly was built in this laboratory from a preliminary design (Fig. 1b) furnished us by Beckman Instrument Company. All parts were machined from stainless steel SAE-52100, especially chosen for its toughness, core hardness and minimum distortion (after heat treatment). After machining, parts were heated to 1525°F, oil quenched and tempered at 350°F for four hours to Rockwell "C" 62-63.

Chemicals

The potassium bromide used here for making the pellets was Baker's analysed reagent grade. Acetone, carbon tetrachloride and carbon disulfide were Mallinckrodt's analytical reagent grade. In addition to Nujol, the mull solvents, hexachlorobutadiene and tetrachlorethylene, and cyclohexane were all Eastman Kodak Company's white label grade.

Pellet preparation technique

Finely divided potassium bromide was prepared by the following procedure:

1. Prepare a saturated solution of potassium bromide.
2. Precipitate the potassium bromide by the slow addition of 200 ml of acetone to 50 ml of the potassium bromide solution.
3. Decant the liquid and wash three times with acetone.
4. After the final decanting, dry the potassium bromide in a clean vacuum desiccator for one week. A vacuum of 100 microns is satisfactory.

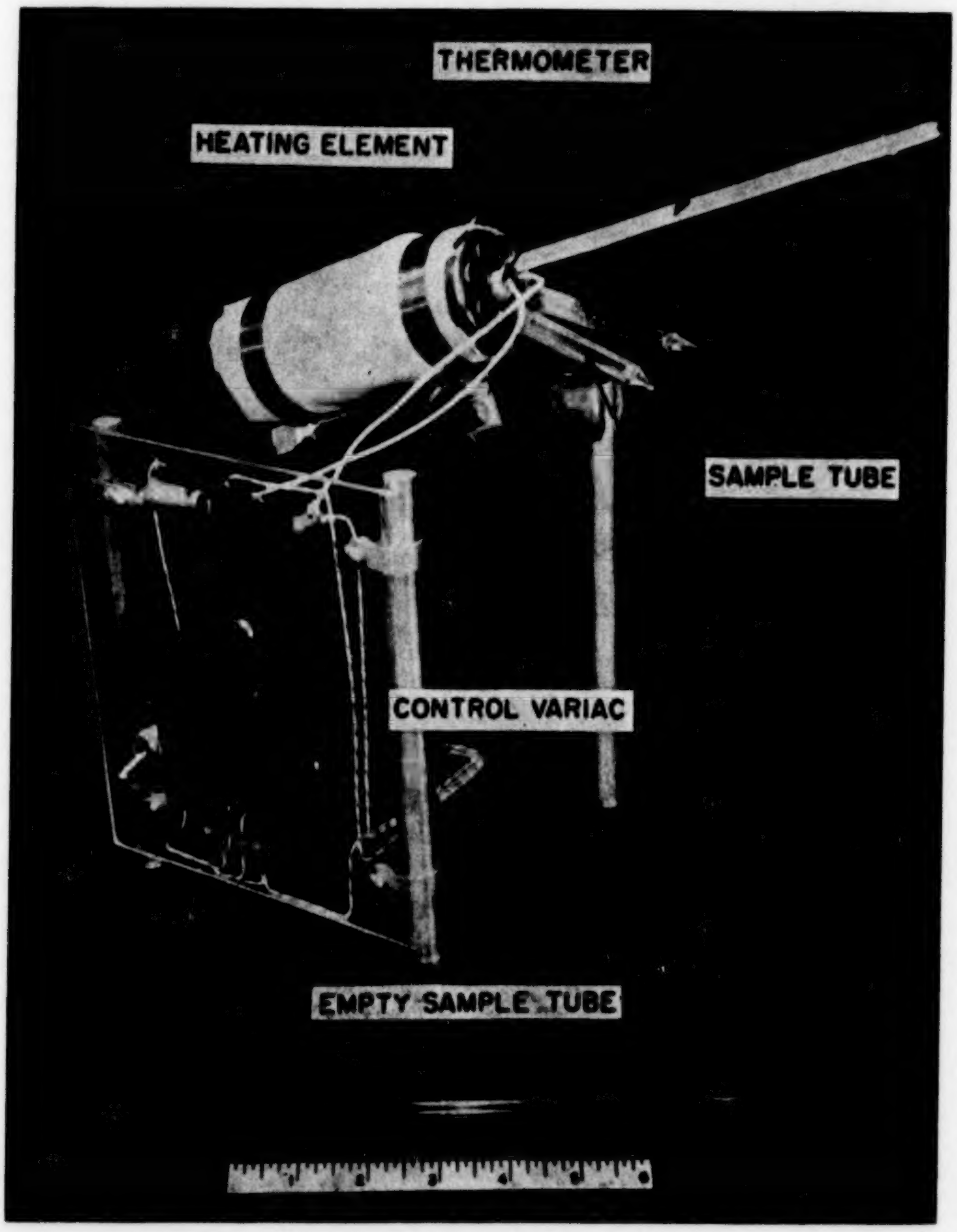

Fig. 2. Furnace apparatus for distillations.

Satisfactory pellets were prepared in the following manner:

1. A blank pellet was obtained by transferring 0.4000 ± 0.0005 g of potassium bromide into a small agate mortar and grinding in the presence of a volatile inert solvent (for example, carbon tetrachloride). The solvent displaces moisture as well as serving as a mull during the grinding operation.

2. The well-ground sample, no longer giving off carbon tetrachloride fumes, is quickly transferred quantitatively to the vacuum die.
3. The material is then tamped into the die with a slightly concave Teflon tamper.
4. The die is then assembled, using a soft aluminum sleeve to keep the plunger from sealing off the port in the collar.
5. A vacuum pump assembly, whose ultimate pressure was below 50 microns, is connected to the assembled die (Fig. 1b) and after approximately 30 minutes pumping, to eliminate all the solvent and air, the sample is subjected to a pressure of 100,000 psi for 30 minutes.

When preparing sample pellets, add the material to be analysed to the potassium bromide and then mix in the presence of the volatile solvent.

Micro-distillation (vacuum)

Because some of the higher boiling materials would interfere with the analysis, a partial separation by distillation was performed. An accurately weighed sample of irradiated material, 25-50 mg, was sealed in a Pyrex tube under a vacuum of 10 microns. The lower part of the tube was heated in a furnace (Fig. 2) for approximately 24 hours. The distillation temperature for *meta*-terphenyl was 115°C and for *para*-terphenyl 160°C. The distillate, collected in the cold end of the tube, was analysed for the parent material.

Due to the presence of an unknown interfering material in the distillate, a better separation of the fractions in the irradiated *ortho*-terphenyl samples was needed. A U-tube, which allows use of a liquid nitrogen cold trap, is used in place of the straight tube as shown in Fig. 2. The interfering volatile fraction condenses conveniently in the cold trap while the remainder of the distillate collects between the end of the heater and the cold trap. The radiation damaged *ortho*-terphenyl samples were distilled at a temperature of 100°C and a pressure of less than 1 micron.

The distilled portion is accurately weighed and then submitted to spectral analysis to ascertain terphenyl content. It is estimated that this analytical micro-distillation method is accurate to ± 3 per cent and that the subsequent spectral analysis by the compressed pellet method is reproducible within ± 1 per cent.

Ultraviolet solution spectra

Ultraviolet absorption analyses (using standard procedures) were made as a check on the pellet infrared method. Solution ultraviolet calibration spectra were determined on 0.1 to 1.0 mg samples of the various terphenyls in 25 ml of cyclohexane. Intensities were determined at several wavelengths for each terphenyl isomer in the region 215 to 350 mμ.

DISCUSSION AND RESULTS

Because the potassium bromide compressed pellet method[4,5,6] is rather new, literature reported techniques and well-founded procedures leading to exacting quantitative analyses are not numerous. For this reason, the quantitative method developed here has been reported in detail, with the hope that it may find application in the analysis of materials other than the polyphenyl compounds of immediate interest.

That various polyphenyls show well-defined and specific absorption peaks in the infrared region has been demonstrated by earlier work[1,2]. Investigations in this laboratory show that quantitative infrared spectrophotometry is possible on these compounds using either the conventional solution technique (Fig. 3) or the newer compressed pellet method. Solubility difficulties make it impossible to determine polyphenyls higher than the terphenyls by solution techniques. In view of this, the compressed pellet method was developed here for determining the various terphenyls with the hope that ultimately quantitative determinations can be performed on the higher polyphenyls by the same method. Spectra of some of the higher polyphenyl fractions isolated from damaged terphenyls have been determined by the compressed pellet infrared method. Until a complete resolution of the various polymer fractions and their molecular weight determinations have been realized, quantitative determinations of these higher polyphenyl compounds by the compressed pellet method are not possible.

It is felt that the compressed pellet method is superior to conventional infrared solution technique for the determination of residual terphenyl in damaged samples because smaller quantities of distillate are needed since substantially all of the pellet is in the beam. Using smaller samples offers the following advantages:

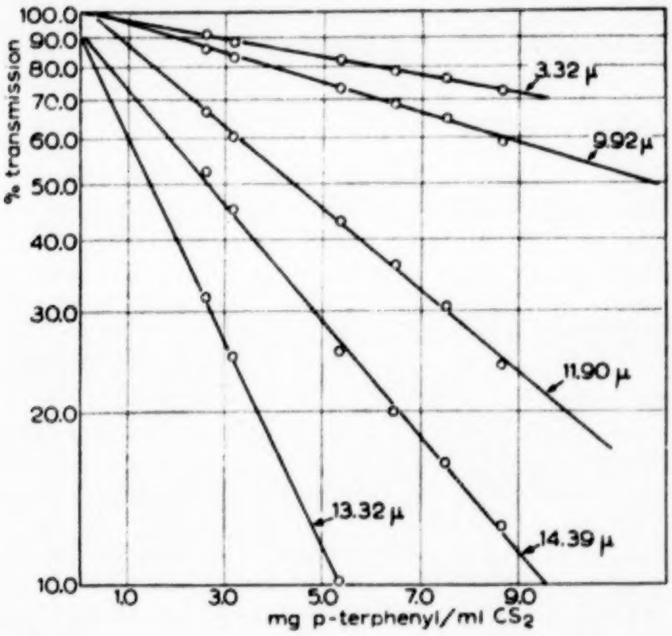

Fig. 3. Spectral calibration curves for *para*-terphenyl in carbon disulfide.

(a) Method especially suitable for analysis of heavily radiation-damaged samples where percentage terphenyl remaining unaltered is small.
(b) Micro-distillation is tedious and leads to poor separation of terphenyl from radiation-produced decomposition products if larger samples are distilled in isolating the terphenyl fraction, and,
(c) When necessary, as little as a few milligrams of damaged terphenyl can be analysed, although ultimate accuracy is less than that achievable with the recommended 25-50 milligram quantity.

That the micro-distillation method described here affects isolation of the terphenyl fraction is seen (Fig. 4) by noting the substantially identical spectra of authentic *meta*-terphenyl and the material isolated by distillation from the damaged sample. A similar correspondence was found with the other terphenyl isomers.

Each of the isomers of terphenyl, containing only small amounts of impurity, can be analysed at any one of several wavelengths (Figs. 5, 6 and 7). In this work the *ortho*-terphenyl was analysed at 12.8 microns, the *meta*-terphenyl at 9.75 microns, and the *para*-terphenyl at 11.92 microns. Mixtures of *ortho*- and *meta*-terphenyl and *ortho*- and *para*-terphenyl can be analysed using these same wavelengths. In samples containing both *meta*- and *para*-terphenyl analysis by this procedure is impossible since the infrared spectrum of either isomer interferes with the other. The effect of residual acetone and/or carbon tetrachloride on the analysis has been eliminated through the use of a blank pellet in the reference beam of the double beam spectrophotometer.

Spectral calibration curves for determination of the three terphenyl isomers by the compressed pellet method are given in Figs. 5, 6 and 7. Pellets produced by this

References p. 258

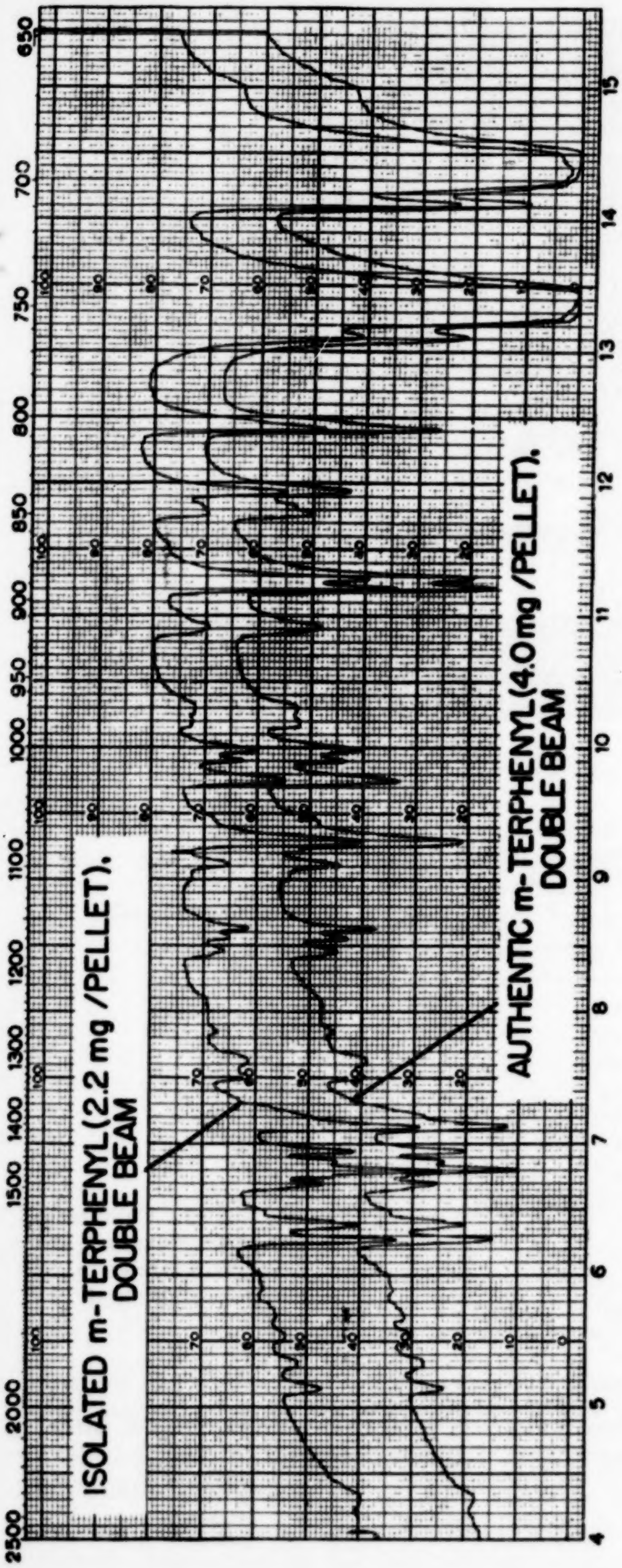

Fig. 4. Comparison of compressed pellet infrared spectra of authentic *meta*-terphenyl and sample isolated from irradiated material by distillation.

method had background transmissions of about 80 to 90 per cent throughout most of the infrared region of interest, 3 to 15.5 μ. The background intensity increases slightly with increasing concentration of polyphenyl. The reproducibility of the pellet method, ± 1 per cent, is approximately the same as that found by conventional solution techniques. The slight deviations from Beer-Lambert's law, noted only in the case of *ortho*-terphenyl, are regular in every instance and do not interfere with the quantitative spectral method, as long as transmission is in the range 10-70 per cent. The deviations might well be caused by shifts in background intensity with variation in concentration of the polyphenyl material.

Poor pellets are produced occasionally because of inadequate dispersion and improper outgassing of the volatile solvent and air. The latter is indicated by a broad absorption in the 9 and 12.5 μ regions and these samples should be rejected. Typical examples of good and bad pellets are shown in Fig. 8.

X-ray diffraction studies on the pellets produced sharp lines indicating that the pellets are polycrystalline in nature. Transmission curves in the short wavelength region of the infrared indicate that particle size of the solid in the pellets usually is less than one micron.

Comparative spectral results, obtained on typically radiation damaged *ortho*-terphenyl samples by the newly developed compressed pellet method and by a conventional solution method based on ultraviolet absorption, are given in Table I. A similar comparison has been made for irradiated *meta*- and *para*-terphenyl

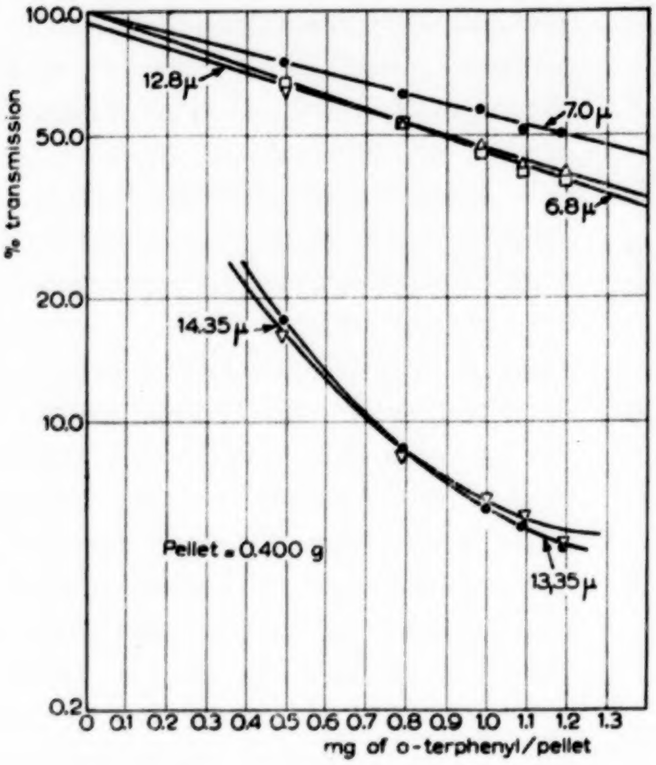

Fig. 5. Compressed pellet spectral calibration curves for *ortho*-terphenyl.

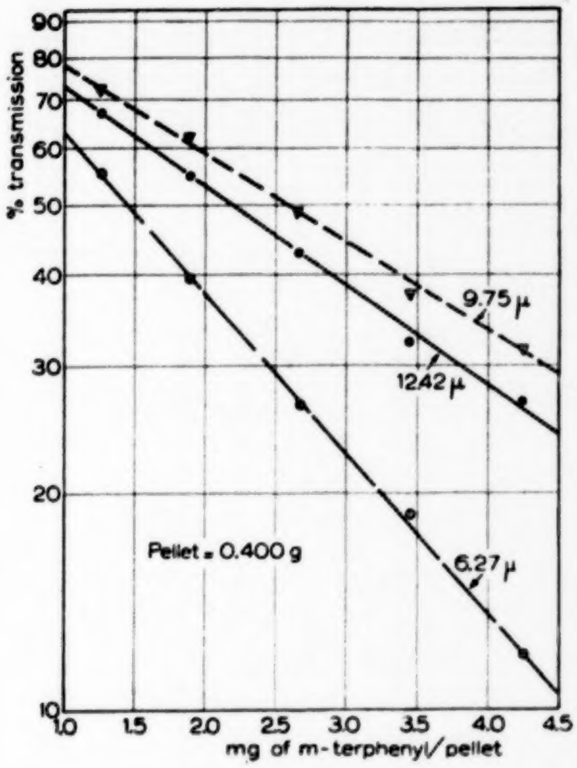

Fig. 6. Compressed pellet spectral calibration curves for *meta*-terphenyl.

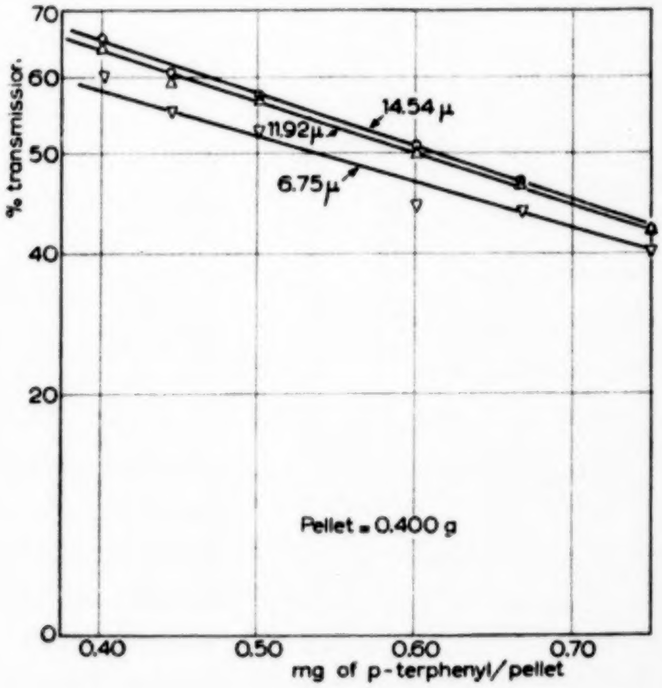

Fig. 7. Compressed pellet spectral calibration curves for *para*-terphenyl.

TABLE I

TYPICAL RESULTS OBTAINED ON IRRADIATED *ortho*-TERPHENYL BY COMPRESSED PELLET I. R. METHOD AS COMPARED WITH SOLUTION ULTRAVIOLET METHOD

Irradiated sample	*% o-Terphenyl* *Soln. U. V.*	*Pellet I. R.*	*% Volatile fraction (Wt. basis)*	*% Polymer (Wt. basis)*	*% Total (Material balance)*	*% Discrepancy*
Electron irradiation[a]	82.8	79.0	6.6	10.7	96.3	—3.7
,, ,,	76.6	74.3	7.4	19.3	101.0	+1.0
Pile irradiation[b]	53.9	52.3	7.1	41.5	100.9	+0.9

[a] Irradiated with 1 Mev electrons at 350°C.

[b] Mixed radiant energy particle irradiated in nuclear reactor.

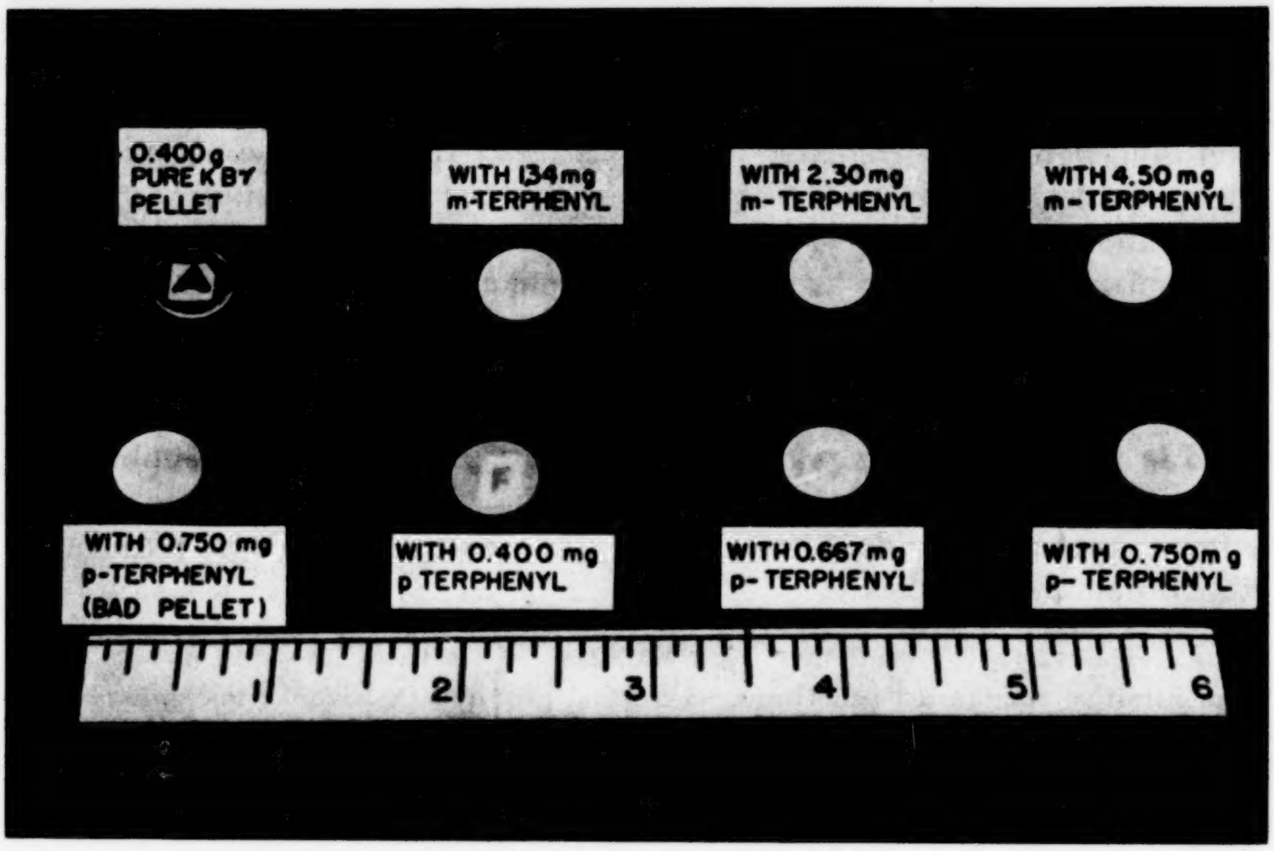
0.400 g
PURE KBr
PELLET
WITH 134mg
m-TERPHENYL
WITH 2.30mg
m-TERPHENYL
WITH 4.50mg
m-TERPHENYL
WITH 0.750 mg
p-TERPHENYL
(BAD PELLET)
WITH 0.400 mg
p TERPHENYL
WITH 0.667mg
p-TERPHENYL
WITH 0.750mg
p-TERPHENYL
1
2
3
4
5
6

Fig. 8. Typical samples of compressed pellets.

TABLE II

TYPICAL SPECTRAL RESULTS OBTAINED ON IRRADIATED *meta*- AND *para*-TERPHENYL SAMPLES

1 Mev electron irradiated sample $\left(\frac{watt\text{-}h}{g}\right)$		*Per cent terphenyl*	
		Solution ultraviolet	*Pellet infrared*
Meta-,	a	80.3	80.0
,,	23.9[b]	71.3	77.9
,,	11.9[c]	63.5	66.6
,,	17.6[c]	56.4	57.9
Para-,	11.8[b]	95.8	95.0
,,	8.6[c]	89.6	91.0
,,	88.4[b]	54.6	56.0
,,	13.5[c]	45.0	43.0

[a] Thermally damaged alone at 450°C.
[b] Irradiated at 400°C.
[c] Irradiated at 450°C.

samples (see Table II). Correspondence of analyses, within no more than about 3% deviation except in one instance, is taken as proof of the reliability of the compressed pellet method developed here for quantitative infrared spectral analysis of polyphenyl compounds.

Spectra (either infrared or ultraviolet) are not specific enough for any one polyphenyl compound to be determined quantitatively in the presence of large quantities of other polyphenyl materials. In the case of the infrared spectra which are more specific than ultraviolet, up to 5 per cent "polymers" (polyphenyls with more than three phenyl rings) will not interfere with quantitative determinations of the terphenyls. Biphenyl and benzene can be tolerated at slightly higher concentrations;

however, these compounds were not found in appreciable quantities in the irradiated terphenyls. The conditions of temperature and time for the micro-distillations, mentioned earlier, in all cases effected a quantitative separation of each particular terphenyl isomer from the irradiated sample within at least 97 per cent. Accuracy of recovery was determined by adding known quantities of pure terphenyls to "polymer" fractions and distilling, etc. Percentage terphenyl obtained by weight alone (separation by micro-distillation) was corrected for minor quantities of impurities based on extent of purity indicated by spectral determination. In all cases, purity of isolated sample of terphenyl was at least 95 per cent.

Results presented here indicate that the compressed pellet infrared method can be used in the analysis of pure or relatively pure terphenyls. When combined with the micro-distillation technique, the method developed for the pure terphenyl isomers was found applicable to identification and quantitative analysis of terphenyls in radiation damaged samples.

SUMMARY

A quantitative compressed pellet infrared method used together with a micro-distillation to effect separation of the isomer has been developed and reported here for the analysis of *ortho-*, *meta-*, and *para*-terphenyl. The terphenyl content is determined on fractions isolated by distillation from radiation dâmaged samples. The compressed pellet infrared method is preferred instead of the more conventional solution technique since smaller quantities of isolated terphenyl are required. The pellet method is applicable also to polyphenyls higher than the terphenyls. The solution technique is not due to the insolubility of the polyphenyls. It is expected that the compressed pellet spectral method developed here might well find application in the analysis of compounds other than polyphenyls. Results presented here appear to be the first quantitative infrared data reported in the literature on polyphenyl compounds.

RÉSUMÉ

Une méthode quantitative infra-rouge, utilisant des tablettes comprimées, combinée à une microdistillation est proposée pour la séparation d'isomères; elle a été appliquée à l'analyse des *ortho-*, *méta-*, et *para*-terphényles. La teneur en terphényle est déterminée sur des fractions isolées par distillation d'échantillons altérés par des radiations. La méthode proposée est plus avantageuse que la technique utilisant des solutions, car elle permet de travailler sur des quantités plus faibles de terphényles isolés. Elle est applicable également à des polyphényles plus lourds, ce qui n'est pas le cas avec la technique en solution, en raison de l'insolubilité des polyphényles. Il semble que cette méthode spectrale (utilisant des comprimés) pourrait s'appliquer à l'analyse de composés autres que les polyphényles. Les résultats donnés semblent être les premières valeurs quantitatives infra-rouges signalées dans la littérature pour les polyphényles.

ZUSAMMENFASSUNG

Zur Trennung von Isomeren wurde eine quantitative Infrarot-Methode (welche komprimierte Tabletten benützt), kombiniert mit einer Mikrodestillation, entwickelt; diese Methode wurde zur Analyse von *ortho-*, *meta-* und *para*-Terphenyl angewendet. Der Terphenylgehalt wird in durch Destillation isolierten Fraktionen von durch Strahlung beschädigten Proben bestimmt. Dieses Verfahren ist dem gewöhnlicheren Lösungsverfahren vorzuziehen, da es kleinere Mengen an isolierten Terphenylen erfordert. Es ist auch für höhere Polyphenyle anwendbar, während dies für das Lösungsverfahren wegen der Unlöslichkeit der Polyphenyle nicht der Fall ist. Wahrscheinlich wird es auch zur Analyse anderer Verbindungen Anwendung finden. Die hier mitgeteilten Ergebnisse scheinen die ersten quantitativen Infrarotangaben über Polyphenylverbindungen in der Literatur zu sein.

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THE ANALYSIS OF COMBUSTION PRODUCTS

V. THE USE OF INFRA-RED SPECTROMETRY FOR FOLLOWING HIGH TEMPERATURE KINETICS*

by

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INTRODUCTION

Attempts to unravel the details of the interaction of molecules of different species in the gas phase can be subdivided into three main groups, both in history and in method. The simplest approach involved the use of some overall property of the reacting system, such as the refractive index or the total pressure, and the measurement of its rate of change with time. This is quite suitable for simple reactions, but abuses were made when the technique was applied to very complicated reactions. The second stage has therefore involved the withdrawal of samples from the system at definite times, and the prevention of further reaction by chilling or diluting. The composition was eventually determined by careful gas analysis, by chemical methods, and, more recently, by mass or optical spectrometry, and by the various forms of chromatography. However, objections can always be made that during the chilling, many extraneous reactions can occur which make the deductions less rigorous. Efforts are therefore now being made to obtain directly information about the processes which take place in the reaction vessel. One method[1,2] has involved withdrawing minute quantities of the reactants through a fine leak into a mass spectrometer. Attention has been drawn, however[3], to the many complications which render the quantitative interpretation of the results a very difficult matter. The use of infra-red spectrometry for studying reactions as they occur in the vessel is still very novel, and this Congress provides a suitable opportunity of considering the potentialities and the problems.

Selection of the infra-red region

Although the U.V. is particularly useful for aromatic compounds, and for those which contain carbonyl groups, it is less applicable for reactions which involve aliphatic hydrocarbons. The latter, and their derivatives, are those with which most pyrolysis and oxidation studies are concerned, and their infra-red spectra are usually sufficiently distinctive for this technique to be considered for following the kinetics.

The use of successive spectra for the study of liquid phase kinetics has been indicated in the Perkin-Elmer literature, but this has not involved any difficulties regarding the vessel. Similar considerations apply to the examination, by rapid scanning with C.R.O. presentation[4], of the spectra of rapid reactions in crossed gas jets, or of the rapid burning of cordite, while the work of BULLOCK AND SILVERMAN[5] was concerned with spark ignited explosions of carbon monoxide-oxygen mixtures in a large vessel, at fairly short wavelengths. The purpose of the present paper is to consider the advantages and the difficulties of following kinetics by examining within the reaction vessel the infra-red absorption spectrum of the reacting mixture. First, the theoretical considerations will be reviewed.

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* Read at the XVth International Congress on Analytical Chemistry, Lisbon, 1956.

THEORETICAL

Effect of temperature on infra-red spectra

The intensity of a single rotational line depends on the relative populations of the states involved and on the transition probability. Assuming thermal equilibrium to be maintained, the fraction of the total number of the molecules in a particular rotational level (J) is equal to $a(2J + 1) \exp(-h^2J(J + 1)/8\pi^2IkT)$, with the usual notation (DALY AND SUTHERLAND[6], referring to CO_2 molecules). At one temperature, the population of the rotational energy levels has been plotted for molecules of various shapes (HERZBERG[7]). It is clear that as the temperature rises, the populations of all the levels change exponentially, but it is not possible to predict quantitatively the effect on the intensity of the bands for a general case. So far, the only problem which has been considered in the literature is that of CO_2[6]. Qualitatively, three formal types of effect may be expected, which are illustrated in Fig. 1.

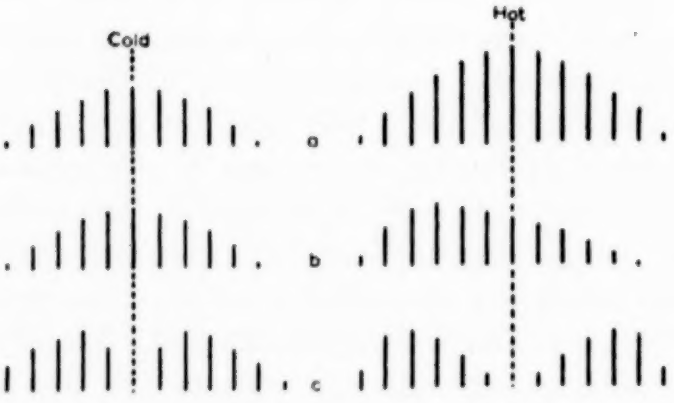

Fig. 1. Possible effects of temperature on intensity distribution of rotational fine structure.

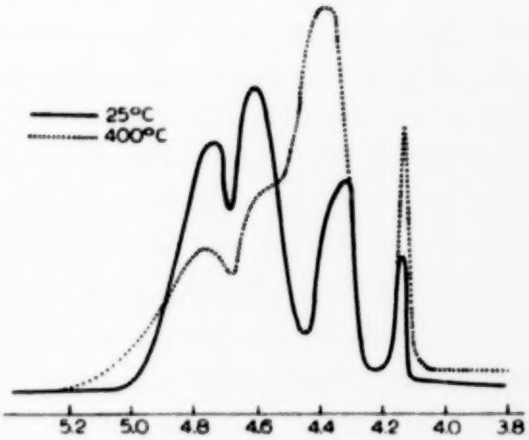

Fig. 2. Effect of temperature on absorption of carbon monoxide and carbon dioxide. Path length 15 cm; composition at 400°C: 380 mm CO; 380 mm CO_2; at 25°C: 154 mm CO; 154 mm CO_2, 452 mm nitrogen.

a) The population of all the levels involved increases; thus the integrated band extinction coefficient increases, with no change in wavelength of the peak of the band. (A decrease in intensity is not impossible.)

b) The population of the higher rotational levels is increased at the expense of that of the lower levels. Both the extinction coefficient and the band maximum change.

c) Similar to case (b), but both in P and R branches. The separation of the maxima increases, and the extinction coefficient changes.

References p. 268

Fig. 2 shows the effects for a mixture of equal quantities of CO and of CO_2 (with equal total numbers of molecules at both temperatures, and the same total pressure). The increase in population of the higher levels of both gases is clearly marked, even though individual lines are not resolved. (N.B. the central portions of the CO_2 band is absorbed by atmospheric carbon dioxide.)

The interaction of absorption with emission was examined by DALY AND SUTHERLAND[6]. They considered a layer l of gas, concentration c, at a temperature T, surrounded by black body radiation at the same temperature. The intensity of emission ($W_{\nu,T}$) in a small solid cone ($\delta\varphi$) across one interface, in the region ν to $(\nu + \delta\nu)$ is given by:

$$W_{\nu,T} = \frac{\delta\varphi}{\pi} E_{\nu,T} \left(1 - \exp(-k_\nu cl)\right)$$

where $E_{\nu,T}$ is the intensity of the black body radiation, and k_ν is the extinction coefficient of the gas at ν,T. It is clear, therefore, (*cf.* Kirchoff's law) that if the absorption is intense, as a result of high values of l or of k_ν, then the emission intensity is also high. It is reduced to zero when there is no absorption. With the CO_2 band at 4.2 μ, k is appreciable even in the gaps between the rotational lines, so that radiation is also important there.

The paper of DALY AND SUTHERLAND, and a brief experimental one by TOURIN[8], appear to be the only ones in the literature. There is an obvious need for a great deal of work in order to provide the necessary data on high temperature absorption and emission.

EXPERIMENTAL

A. Instrumentation

1. *The spectrometer*

The double-beam spectrometer has been described elsewhere[9], but the optical path is shown below.

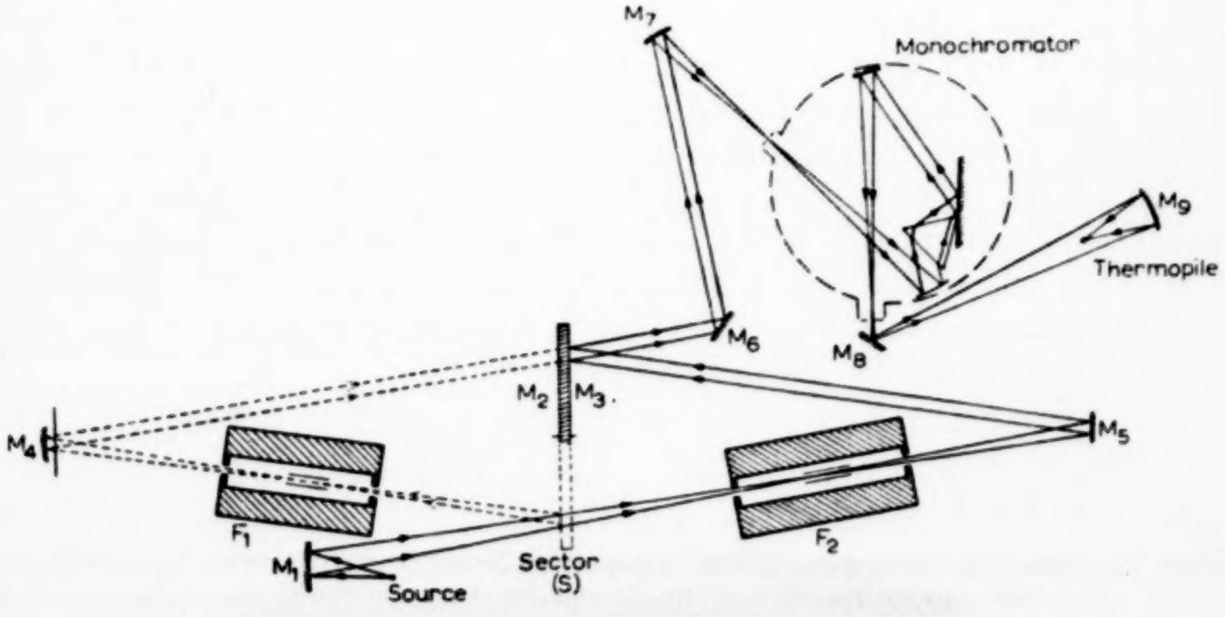

Fig. 3. Optical path of spectrometer.

Light from a Nernst filament passes alternately through two cells at F_1 and F_2, and later follows a common path into the Wadsworth monochromator. The latter has a calcium fluoride prism, and the H_2O peaks at 1671 and 1676 cm^{-1} can easily be resolved. The signal from a Schwartz thermopile is fed into a tuned, 4-cycle amplifier, which detects and amplifies the difference in the light emerging from cells F_1 and F_2. For some purposes, the difference is rectified electronically and fed to a pen recorder ("pen" mode of operation); an alternative is to use a mechanical, phase sensitive, rectifier in conjunction with a servo unit to operate a compensating shutter across mirror M_4, which also indicates the percentage absorption on a recorder ("servo" operation). The spectrometer was constructed with two furnaces around the cells at F_1 and F_2, together with pumping and filling lines and associated equipment.

2. *Windows*

A special reaction vessel has been designed, through which infra-red radiation can be passed while the cell is mounted in the furnace. The material of which the cell is constructed must have no catalytic or other effect on the course of the reaction; the choice for the body of the cell is therefore restricted to pyrex and silica.

Window materials such as rocksalt, or potassium bromide, are normally used for infra-red spectrometry at room temperature. At higher temperatures, difficulties arise in joining the windows to the cell body; they must be sealed so that the cell is vacuum tight throughout the range of temperature which is likely to be used, *i.e.* 250-520°C (or higher if a silica tube is used instead of pyrex). Rocksalt can be cemented to pyrex with fused silver chloride (m.p. 455°C), but owing to their widely different coefficients of expansion, the seal is only stable when the cell is maintained at the high temperature. On cooling, the rocksalt end-plates are found to fracture. This difficulty can be overcome if a sleeve of silver is interposed between the windows and the glass[10], and is sealed to both with silver chloride. The elasticity of the metal sleeve then permits the two parts to contract independently on cooling. Unfortunately, silver has a powerful surface effect on the course of oxidation reactions.

Another approach involves the use of some flexible seal between the rocksalt window and the cell material. These are clamped together under spring pressure to obtain a vacuum tight joint. Silicone grease can be used for this purpose up to a temperature of 300°C for a short time. Above 250°C, polymerisation of the silicone material occurs, which leads to hardening and, in time, to leakage of the seal.* Furthermore, at high temperatures, this substance absorbs considerable quantities of hydrocarbons. Silicone rubber and Teflon (polytetra-fluoroethylene) were also tried as sealing materials. However, both of these evolved vapours which absorbed in the infra-red region and had a detectable vapour pressure. This indicated that partial decomposition took place below 300°C. Some other technique is thus required, which does not involve the use of alkali halide windows.

Two materials are available which can be joined to pyrex by graded seals. Of these, quartz has too limited a transmission, which restricts the range of the method. Sapphire was found to be satisfactory, however, and the reaction vessel was finally constructed with windows of this substance. A transmission curve shows that it is now possible to operate as far as 6.5 μ.

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* Since this communication was written, a paper by NEU (*J. Phys. Chem.*, 60 (1956) 320) has appeared which describes hydrocarbon oxidation studies at *ca.* 270-280°C, also using silicone grease to join rocksalt windows to a pyrex body. NEU reports an upper useful limit of temperature coincident with ours.

The sapphire end-plates were synthetic ones produced by the Salford Electrical Co., and they were joined to pyrex through a multiple graded seal by British Thomson-Houston, Rugby. Owing to the difficulties of manufacture and of sealing, the widest windows obtainable were $\frac{1}{2}''$ diameter (after sealing). This considerably decreases the amount of light which can be passed through the cell, but there are several compensating advantages. The reaction vessel is now a robust unit, with no troublesome seals. It is completely resistant to water, which is one of the main reaction products, and might well attack halide surfaces. Again, oxidation systems are particularly sensitive to the presence of alkali halides, while fused alumina is likely to be more inert. A reproducible surface is easily obtained with a vessel of the present design, since it can be subjected to the normal cleaning techniques (such as treatment with hydrofluoric acid) under carefully controlled conditions. Finally, the very high melting point of sapphire practically eliminates any high temperature limitations on the use of the windows.

Mention must be made of periclase, crystalline magnesium oxide, which transmits up to 9.5 μ and has the same coefficient of expansion as steel. Wide periclase windows are now available, which can be clamped rigidly to steel tubes, using soft metal gaskets. However, the presence of metal surfaces prohibits the use of a cell of this type for oxidation studies.

3. *Furnace considerations*

The present work was concerned with reactions between 250°C and 430°C. At these temperatures complications are introduced by the emission from the furnace, cell and hot gases. The pre-chopping technique adopted in infra-red flame studies[11,12,13] eliminates the problem by letting the emitted light reach the detector continuously, the signal then being lost in the tuned a.c. amplifier. However, this can only be done with single beam operation, since with double beam systems, some alternation of light beams is necessary at a later stage to collect the light beams into a common path (see below).

It was found, at 420°C, that the emission from the furnace and empty cell had half the intensity of the Nernst filament at 1600 cm^{-1}, and decreased continuously to one-hundredth at 3300 cm^{-1}. Since the peak emission of a black body at 420°C should be in the region of 3.6-4 μ, the extra radiation must be associated with the increasing absorptivity (and hence emissivity) of the sapphire windows. If rocksalt plates could be used, then presumably the same effect would be noticed even more strongly at long wavelengths since, in the region of its cut-off wavelengths (14-16 μ) the black body radiation curves are very much closer to each other than at 5-6 μ.

The presence of strongly absorbing gas in the cell with sapphire windows can increase the emissivity until the latter approaches the value of unity. Under these conditions, the movement of the servo shutter obscures not only light from the Nernst source, but also some of the radiation from the furnace, cell and contents at F_1. The percentage indicated is thus falsified, and the effect is in such a direction that the deflection for 0-100% on the recorder paper is decreased. This considerably reduces the precision of any determinations, and, indeed, the usefulness of the system.

Some improvement would be possible if the servo shutter were to cross the beam before it entered the furnace, but the fundamental problem is presented by the chopping of the emission from the furnaces. If the two light beams entered the common path in the monochromator in a system which permitted the chopping to take place before the entrance of the furnaces, then no difficulty would arise. These requirements cannot be met by double-beam spectrometers of conventional design. It is therefore necessary to use the "pen" mode of operation, and to measure the difference in intensity of the two light paths.

B. Applications

At low temperatures, when emission presents no problems, the servo method may be used provided sufficient sensitivity is obtained, and also that the band studied initially has a transmission in the vicinity of 40% (see A. E. MARTIN[14] for discussion of factors affecting precision). Should the band be stronger, with no possibility of reducing the pressure or the cell length, then a smaller change in its intensity may, in many cases, be expected. It is then possible to introduce enough of the appropriate compound so that balance is obtained after the completion of the partial reaction. An increase of transmission from 5% to 10% say, could then be made to correspond to full scale deflection. This is particularly useful for following a partial oxidation.

If there is strong interference, exact compensation can only be made at one composition, as was done by NEU, for example, to estimate the end-products of butane oxidation. For continuous changes, this technique could only be used on a point-by-point basis, if independent bands are present to permit the deduction of the concentration of the interfering compound. However, if for any reason the major absorption should remain relatively unchanged, useful semiquantitative results could be obtained by compensating in the comparison beam.

At higher temperatures, where the "difference-pen" technique must be used, the effect of an intense overlapping band (A) is manifested at all times, since the deflection is now more directly related to the concentration of the compound under investigation (X) than the transmission measured by the servo unit. Small changes of (A) now have as much influence on the output as does the increase in (X). On the other hand, if the absorption of (A) is low relative to that of (X), then the presence of a suitable concentration of (A) in the reference beam will reduce the interference caused by the changes in (A), and emphasise the absorption due to (X).

For any particular problem, the choice of method is guided by the sensitivity required.

1. *Selection of spectral region*

In the partial oxidation of propane, at the relevant temperatures, the products of interest are those containing carbonyl groups, carbon monoxide, and propylene. The concentration of carbonyl compounds, consisting mostly of aldehydes, is easily deduced by using the broad 1720-1740 cm^{-1} band, interference by water and by propane being small due to their weak absorption. Furthermore, the low-frequency C-H stretching band at *ca.* 2700 cm^{-1} is characteristic of aldehydes, but, like the propylenic band (see below), this is affected by the disappearance of the propane, which, in this region, absorbs considerably.

The measurement of carbon monoxide concentration can be effected at 2120 and 2170 cm^{-1}. The latter is more useful since it is slightly more intense, and since more energy is available from the source. However, if carbon dioxide is also one of the products, then its absorption interferes sufficiently, particularly at high temperatures (Fig. 2), to make it necessary to use the 2120 cm^{-1} band. Thus in the partial oxidation of propane, the 2170 cm^{-1} band can be used in the "high temperature" regions, above 405°C (the present conditions), since very little CO_2 is formed. The change in intensity caused by the disappearance of the propane is found to be negligible, (to within 2%).

Since the region above 6.5 μ was cut off by the sapphire windows, the propylene bands which might be considered included those at 1651 cm^{-1}, 1825 cm^{-1} and 3100 cm^{-1}. The intensity of the former was halved by the absorption of the windows, and interference was found from the absorption of propane and of atmospheric water vapour. The 1825 band was also interfered with by the carbonyl bands and by water. Neither band was particularly sensitive, some hundreds of mm pressure of propylene being needed to provide a signal large enough to permit accurate measurement of the kinetics.

The $=C-H$ stretching band at 3089 cm^{-1}, which was much more intense, occurred at the minimum in the propane "window", *i.e.* between the bands at 2938 and 3138 cm^{-1}. In the presence of a ten-fold excess of propane, however, the propylene band was barely visible when the double-beam "servo" method was used, with no propane in the comparison cell at F_1. Even with an equal quantity of propane in the latter, only a small peak could be obtained. When the "difference-pen" mode of operation was used instead, it was found possible to increase both slit width and amplifier gain until no further improvement could be made. Under these conditions, a deflection of 70% of f.s.d. was produced at 400°C from 50 mm propylene, which was adequate, although this sensitivity could be increased by a factor of *ca.* 3× if it were not necessary to use windows of only 0.5 inch diameter.

The interference due to the disappearance of propane, however, made it impossible to calibrate more than semiquantitatively for propylene. Nevertheless, useful information has been obtained by the use of this band.

2. *Operating pressure*

In view of the effect of pressure on the intensity of absorption, which is particularly important for instance with carbon monoxide, the total initial pressure in both cells was fixed at 760 mm. The partial pressure of propane was also equal in both cells; the remaining gas in the comparison cell being nitrogen. In many experiments, the required mixture composition was obtained by admitting air to the reaction vessel until atmospheric pressure was reached. Mixtures of propane and oxygen, however, were made up in a separate vessel, and then introduced together.

3. *Procedure*

With both cells filled with the same mixture of propane and nitrogen at 760 mm, the slits are opened to the appropriate setting and the residual signal is reduced to nearly zero by a small movement of mirror M_4. Slightly more light is allowed to reach the thermopile from cell F_1 than from cell F_2, and the final balancing of the two beams is then effected by moving a fine wire across the entrance to furnace F_2. This operation is very critical, since the signal from either side is four to six times greater than full scale deflection, and the out-of-balance signal must be less than 1% of f.s.d.

The thermopile is then hooded and the cell at F_1 is evacuated by pumping for a set time. It is then filled with the reaction mixture, the hood is removed and the recorder chart is started. The almost instantaneous heating of the gas admitted to the reaction vessel is indicated by the pressure on a mercury manometer connected to the closed system, a steady value being reached in less than one second. At the end of the first run, the 2170 cm^{-1} region is scanned slowly, with narrower slits, and the prism drive is stopped at the position of maximum signal. This position is used in all subsequent work. The slit widths and gain are both increased until a reasonable signal is obtained, of *ca.* 70% of f.s.d.

Calibration for response to carbon monoxide, for example, is carried out after every run. With the thermocouple hooded, the vessel is evacuated, and a small amount of carbon monoxide is admitted. This is followed by the same quantity of propane as is present in the comparison cell, and then by nitrogen; a short time (*ca.* ½-1 minute) is necessary for mixing to become complete, since the carbon monoxide is initially driven to the ends of the tube by the much larger quantity of propane and of nitrogen. The deflection is then recorded. The vessel is then evacuated (with the detector hooded) and the procedure is repeated several times with different partial pressures of carbon monoxide.

When a number of duplicate experiments were carried out, the total quantity of carbon monoxide formed was always within 1% of the mean. The individual *p-t* curves were usually indistinguishable when plotted on a common graph, and the individual slopes agreed to within 3%. A typical graph of the formation of carbon monoxide pressure-time curve is shown in Fig. 4.

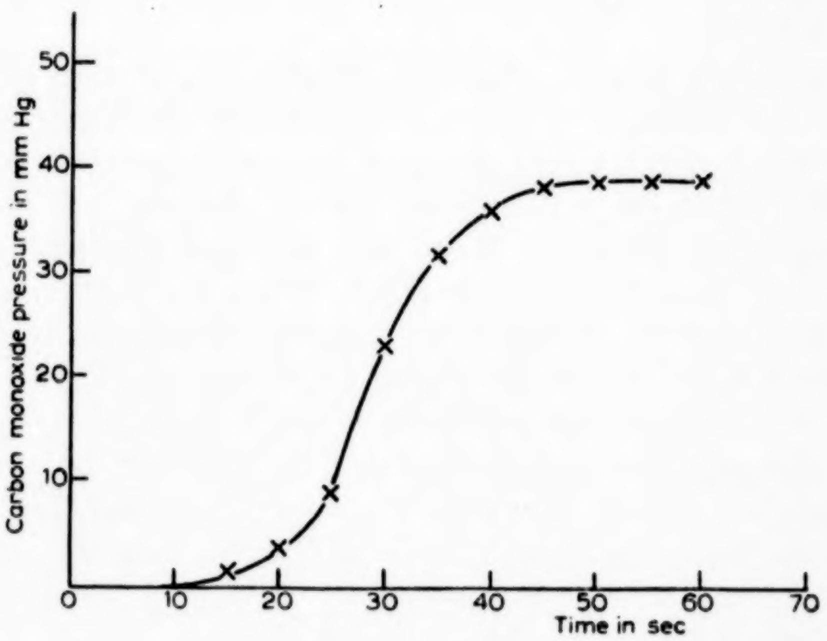

Fig. 4. Typical graph of formation of carbon monoxide during slow oxidation of propane at 411°C. Partial pressure of air: 380 mm. Partial pressure of propane: 380 mm.

DISCUSSION

The present work has shown that high temperature gas phase kinetics can be followed *in situ* with considerable precision by recording the infra-red absorption at a particular wavelength. The method described for propane can be simply adapted so as to permit the study of the rate of formation of carbon monoxide, carbon dioxide (though this is complicated by atmospheric absorption), aldehydes and other compounds. Extensions to higher temperatures are clearly possible, for example with silica cells fitted with sapphire windows. Emission effects, however, would require considerable control if they are not to falsify the information obtained experimentally. At sufficiently high temperatures, it may even be more convenient to measure concentrations by using emission instead of absorption bands.

One of the chief advantages lies in the automatic recording of the results. This makes it very convenient for following fast reactions, and in fact, many of the runs reported here lasted less than 12 seconds. The limit is set mainly by the speed of response of the detector, and by the characteristics of the amplifier. The former could be increased considerably by the use of photoconductive cells; these are more sensitive than the Schwarz thermocouples, so that better resolution can be obtained, and hence a further improvement in the limit of detection. Recorders fast enough to register the information are already available. It is therefore clear that it is now possible to investigate the hitherto neglected range of kinetics which lies between the static and the flow methods. The former is usually concerned with runs lasting more than 2 minutes, while the latter is more suitable for short contact times. The advantages of the cell with sapphire windows have already been described, but the reproducibility of the results obtained support the claims made for the stability and inertness of the windows.

SUMMARY

For the detailed elucidation of reaction mechanisms it is not adequate merely to stop a reaction at various times and to analyse the resulting products as a function of time, since many side reactions may occur during chilling. More reliable deductions could be made if the variation with time of the concentration of individual reactants could be determined within the reaction vessel at the reaction temperature. The purpose of the present communication is to discuss the possibility of using infra-red spectrometry for this purpose.

A number of problems are encountered in the application of the technique: it is found, for example, that only certain types of double beam spectrometers can easily be used. A special, sensitive method is finally described for following the formation, *in situ*, of carbon monoxide and other compounds in the slow oxidation of propane. The advantages and the possible applications and improvements are discussed in detail.

RÉSUMÉ

Pour une étude détaillée des mécanismes de réaction, il n'est pas suffisant seulement d'arrêter une réaction à différents temps et d'analyser les produits obtenus en fonction du temps, puisque plusieurs réactions secondaires peuvent se produire pendant le refroidissement. Des déductions plus plausibles pourraient être faites si la variation de la concentration en fonction du temps pouvait être déterminée dans le récipient où se fait la réaction, à la température de la réaction. Le but de ce travail est d'examiner la possibilité d'utiliser la spectrométrie infra-rouge pour ces recherches.

Un certain nombre de problèmes se sont posés dans l'application de cette technique; on a constaté, par exemple, que seulement certains types de spectromètres à double faisceau peuvent facilement être utilisés. Une méthode spéciale, sensible, est finalement décrite pour suivre la formation *in situ* de l'oxyde de carbone et d'autres composés dans l'oxydation lente du propane. Les avantages, les applications et les perfectionnements possibles sont discutés en détail.

ZUSAMMENFASSUNG

Für eine eingehende Aufklärung des Reaktionsmechanismus genügt es nicht, die Reaktion einfach zu verschiedenen Zeitpunkten zu unterbrechen und die Reaktionsprodukte als Funktion der Zeit zu analysieren, da beim Kühlen viele Nebenreaktionen auftreten können. Zuverlässigere Schlüsse könnten gezogen werden, wenn die Änderung der Konzentration der einzelnen reagierenden Stoffe innerhalb des Reaktionsgefässes und bei der Reaktionstemperatur bestimmt werden könnte. Zweck dieser Mitteilung ist es, die mögliche Anwendung der Infrarot-Spektrometrie zu diesem Zwecke zu erörtern.

Bei der Anwendung dieser Technik begegnet man einer Anzahl von Schwierigkeiten; so findet man, zum Beispiel, dass nur gewisse Typen von Spektrometern mit doppeltem Strahlenbündel leicht verwendet werden können. Eine spezielle, empfindliche Methode wird schliesslich beschrieben, um die Bildung, *in situ*, von Kohlenmonoxyd und anderen Verbindungen bei der langsamen Oxydation des Propans zu verfolgen. Die Vorteile und die möglichen Anwendungen und Verbesserungen werden ausführlich erörtert.

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RAPID SPECTROPHOTOMETRIC DETERMINATION OF COPPER IN IRON, STEEL AND FERROUS ALLOYS

by

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Wetlesen and Gran[1] have proposed a new method for spectrophotometric determination of copper in pulp and paper using bis-cyclohexanone-oxalyldihydrazone as reagent. This reagent was found to be highly specific for copper. Peterson and Bollier[2] later used the reagent for the determination of copper in blood serum.

The present work deals with the application of this reagent for the determination of copper in iron, steel and ferrous alloys.

EXPERIMENTAL

Apparatus and special reagents

Spectrophotometer. A Beckman Spectrophotometer, model B, with 1-cm cells was used.

Citrate buffer solution. Dissolve 75 g citric acid in 100 ml distilled water. Add 95 ml concentrated ammonium hydroxide and dilute to 250 ml.

Reagent solution. Dissolve 0.5 g bis-cyclohexanone-oxalyldihydrazone in 100 ml of hot 50% alcohol. The solution is stable for 3-4 months. If the reagent crystallizes out on standing, warm to redissolve the crystals.

Indicator solution. Neutral red, 0.1% solution.

Procedure

Dissolve a 1-gram sample in 25 ml sulfuric acid (1+9) and 15 ml nitric acid (1+9). After the reaction has ceased, boil to expel oxides of nitrogen. Filter the solution and dilute to 100 ml in a volumetric flask. Transfer a 5 ml aliquot to a 50 ml volumetric flask, add 10 ml of buffer solution and one drop of neutral red indicator. Add ammonium hydroxide until the indicator turns yellow. Add two or three drops in excess. Then add 5 ml reagent solution. After two minutes make up to volume with distilled water and read the absorbance of the blue copper complex formed at 595 mμ.

References p. 270

To compensate for the color produced by iron and alloying elements with citric acid, prepare a correction solution treating another 5 ml aliquot in the same way, but without the addition of reagent. Read the absorbance of this solution at 595 mμ.

For steel alloys which are not dissolved in sulfuric and nitric acid:
Dissolve in *aqua regia*, add perchloric acid and evaporate to fumes.
Dilute with distilled water and filter. In the spectrophotometric determination the above procedure is used without change.

Effect of variables

Effect of pH

In the absence of foreign metals the blue copper complex is formed in the pH range 7.5-9.5. In the presence of iron, however, the optimum pH range is between 8.0 and 9.5. At pH below 8.0 and above 9.5 the absorbance is appreciably lower.

Effect of buffer concentration

A comparatively high concentration of buffer is required in order to avoid precipitation of certain foreign metal hydroxides. If the buffer concentration is not sufficiently high, the presence of some metals sometimes delays the formation of the blue copper complex. Accordingly the reagent should be added before the solution is diluted.

Effect of amount of reagent

Five ml of the reagent solution were found to be sufficient to obtain optimum absorbance. Excessive amounts of the reagent did not influence the absorbance.

Effect of temperature

Reproducible results were found in the temperature region 15-50°C. Raising the temperature above 50°C caused a fading of color. Below 15°C the formation of the copper complex was sometimes delayed.

Effect of standing

In the absence of large amounts of foreign cations the color is stable for hours. The stability of the color is however affected by the presence of other cations, but usually it is stable for at least one hour. In the presence of nickel and cobalt the color is stable for only five to ten minutes.

Sensitivity

The molar absorbtivity (e) was found to be 16.000, or log $e = 4.218$.

Effect of other ions

Bis-cyclohexanone-oxalyldihydrazone was previously stated to be highly specific for copper in the presence of comparable amounts of other ions[1]. The negative interference caused by some cations reported by PETERSON AND BOLLIER[2] is overcome by the use of high citrate buffer concentration.

Although iron does not react with bis-cyclohexanone-oxalyldihydrazone it does produce a color with ammonium citrate. This is corrected for by use of a blank solution, the preparation of which is described earlier. The effect of the alloying elements, most common in steel, was examined in concentrations about hundred times that of the copper concentration. The concentration of iron in these investigations was about five hundred times the copper concentration. The method employed for examining these effects was the same as in the outlined procedure except that the foreign ions were added to a small volume of standard copper solution. The determination of copper was satisfactory in the presence of manganese, vanadium, titanium, molybdenum, tungsten, niobium, tantalum and hexavalent chromium. Trivalent chromium was precipitated even in the presence of citric acid and must be oxidized to the hexavalent state. Large amounts of nickel caused negative interference and the color was not stable for more than five minutes. Large amounts of cobalt also caused negative interference. Nitrate, sulfate, chloride, phosphate and perchlorate did not interfere.

Representative results for copper determination in National Bureau of Standard samples are listed in Table I.

TABLE I

DETERMINATION OF COPPER IN NATIONAL BUREAU OF STANDARD SAMPLES

Sample No.	*Identity*	*Copper present* %	*Copper found* %
6E	Cast iron	0.254	0.258
4g	Cast iron	0.240	0.245
73a	Steel, 14% Cr	0.080	0.080
50b	Steel, 14% Cr, 18% W	0.110	0.117
153	Steel, 8% Mo, 8% Co, 4% Cr, 2% V	0.099	0.096
11f	Steel, Basic, Open Hearth	0.098	0.095
121b	Steel, 18% Cr, 8% Ni	0.124	0.123
106a	Steel, 1% Al, 1% Cr	0.156	0.153
126a	Steel, 36% Ni	0.092	0.070

SUMMARY

A rapid spectrophotometric method for the determination of copper in iron, steel and ferrous alloys without separating the copper has been developed. The sample is dissolved in acid and ammonium citrate is added to complex the iron and other alloying elements. The pH is then adjusted to 8.0-9.5 with ammonium hydroxide. A solution of bis-cyclohexanone-oxalyldihydrazone is finally added and the absorbance of the blue copper complex formed is measured.

RÉSUMÉ

Une méthode spectrophotométrique rapide est proposée pour le dosage du cuivre dans le fer, l'acier et les alliages ferreux, sans séparation préalable. On dissout l'échantillon dans un acide et on ajoute du citrate d'ammonium pour complexer le fer et d'autres éléments de l'alliage. On ajuste le pH entre 8.0 et 9.5 par addition d'ammoniaque et on ajoute finalement une solution de bis-cyclohexanone-oxalyldihydrazone. On mesure l'absorption du complexe bleu de cuivre formé.

ZUSAMMENFASSUNG

Eine schnelle spektralphotometrische Methode für die Bestimmung von Kupfer in Eisen, Stahl und Eisenlegierungen ohne Abscheidung von Kupfer, wurde entwickelt. Die Probe wird in Säure gelöst und zitronsaures Ammonium wird zugefügt, um Eisen und andere Legierungselemente zu komplexieren. Hierauf wird das pH mit Ammoniak auf 8.0-9.5 eingestellt. Schliesslich wird eine Lösung von bis-Cyclohexanon-oxalyldihydrazon zugefügt und die Absorption der geformten blauen Kupferkomplexverbindung gemessen.

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COULOMETRIC TITRATION OF ANTIMONY WITH ELECTROGENERATED IODINE

by

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Electrogenerated iodine has been employed for the coulometric titration of +3 arsenic[1,2,3], thiosulfate[4,5], sulfide[6], and selenite[7]. The present study extends the application of coulometric titrations with iodine to the determination of +3 antimony.

A coulometric titration of tripositive antimony in hydrochloric acid medium with electrogenerated bromine has been described by BROWN AND SWIFT[8,2]. Using amperometric end-point detection the bromometric titration yields excellent results, but, according to our experience, it is not amenable to potentiometric e.p. indication. The iodometric titration can be performed with potentiometric, amperometric, or visual e.p. indication, and it is applicable in the presence of substances (*e.g.*, many organic compounds) which would interfere with a bromometric titration.

EXPERIMENTAL

The optimum solution conditions for the coulometric iodometric titration of tripositive antimony are, of course, the same as for titration in the classical manner; in particular, the pH of the solution must be between about 7 and 9, and a complexing agent (*e.g.*, tartrate ion) must be present to prevent hydrolytic precipitation of the antimony. In the coulometric titration of arsenic RAMSEY, FARRINGTON AND SWIFT[3] observed that removal of dissolved oxygen was necessary, but we found that this was unnecessary in the titration of antimony.

The supporting electrolyte consisted of a $0.1M$ phosphate buffer of pH = 8 containing $0.1M$ potassium iodide, and $0.025M$ potassium tartrate.

The titration cell (70 ml weighing bottle) was similar to that described by MYERS AND SWIFT[9], except that magnetic stirring was used and the generator cathode (platinum wire coil) was isolated from the test solution by enclosure in a glass tube with a sintered glass bottom. The generator anode was perforated platinum foil with an area (one side) of 8.4 cm^2. The amperometric indicator electrodes were platinum foil with an area of 1.6 cm^2 each. For potentiometric e.p. detection one of these electrodes was used as indicator electrode in combination with a saturated calomel reference electrode.

The constant (± 0.01%) electrolysis current was supplied by the regulator previously described[10], and was selected with respect to the quantity of antimony to provide titration times in the 100-500 sec range. Time was measured with a Standard Electric Time Co. Model S-10 clock (1000 sec range and ± 0.01 sec reading error), driven by the local public utility power supply whose short term frequency variation was within ±0.15%.

Known quantities of antimony were taken in the form of a standard potassium antimonyl tartrate solution, whose titer was established by iodometric titration in the ordinary way. Blank titrations with the supporting electrolyte alone were performed at each current level, and the resulting small correction was deducted from the observed titration time.

Performance data

Table I summarizes the results of titrations of 60 µg to 10 mg quantities of antimony in a volume of about 50 ml, using both amperometric and potentiometric end-point detection.

TABLE I

PERFORMANCE DATA

The supporting electrolyte was a 0.1*M* phosphate buffer of pH = 8, containing 0.1*M* potassium iodide, and 0.025*M* potassium tartrate, and the volume was *ca.* 50 ml. Electrolysis currents ranging from 2 to 33 mA were used to yield titration times between 100 and 500 sec.

No. of trials	*Sb taken µg*	*Sb found (av.) µg*	*Average deviation µg*	*Average error %*	*End-point detection*
5	65.55	66.00	± 1.6	+0.7	Amp.
7	327.8	327.6	± 1.0	—0.1	,,
3	1311	1311	± 1.0	0.0	,,
4	10,450	10,530	±10	+0.8	,,
4	65.55	65.14	± 0.7	—0.6	Potent.
4	327.8	328.3	± 0.2	+0.2	,,
3	1311	1311	± 1.3	0.0	,,
4	7768	7774	± 3.0	+0.1	,,

Because the iodine-iodide couple functions with very little overpotential in either direction, whereas the antimonous-antimonic couple behaves quite irreversible, the amperometric indicator current remains very small up to the equivalence point and then increases rapidly due to depolarization of the indicator cathode by the excess iodine. Fig. 1 shows a typical amperometric titration curve. In practice generation of iodine is continued far enough to define the slope of the titration line beyond the e.p., and the latter is then determined by back extrapolation. Provided it is kept constant the voltage applied across the indicator electrodes is not very critical. A value of 150 mV was used, but equally satisfactory results doubtless could be obtained at other values in the 50 to 300 mV range.

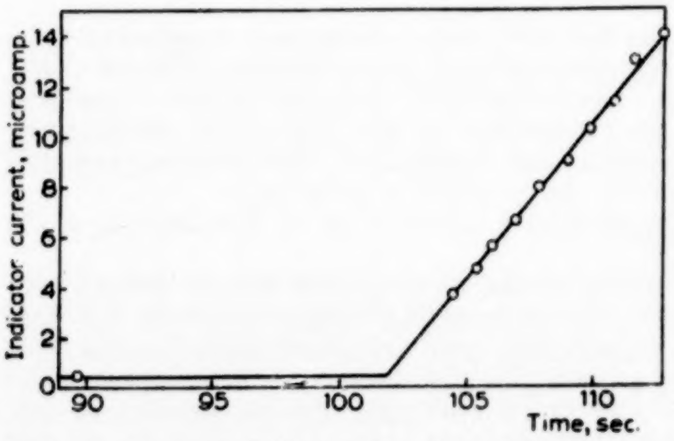

Fig. 1. Amperometric end-point detection in coulometric titration of 327.8 micrograms of antimony with a generating current of 5.151 mA, and with 0.150 V impressed across the two platinum indicator electrodes.

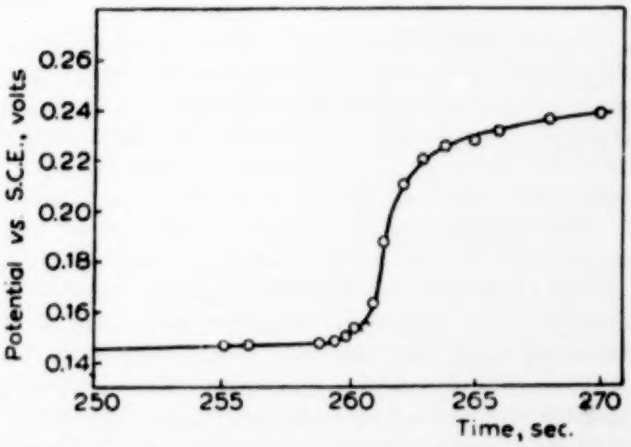

Fig. 2. Potentiometric end-point indication in coulometric titration of 1.311 mg of antimony with a generation current of 7.961 mA.

Potentiometric e.p. detection followed the usual practice[2], and a typical titration curve is shown in Fig. 2. The titration curve displays the assymetry expected from the assymetrical nature of the iodine-iodide half-reaction. Steady potentials are established very quickly, so that the titration can be completed rapidly simply by interrupting the generating current when the end-point potential (+0.18 V *vs.* S.C.E.) is reached.

The data in Table I show that the precision (average deviation) and accuracy (average error) of both e.p. detection techniques are comparable with the intermediate quantities of antimony. However with both relatively small (< 100 microgram) and relatively large (> 5000 microgram) amounts of antimony potentiometric detection tends to be both more precise and more accurate than amperometric detection. Potentiometric detection is also more convenient because it permits direct titration to a reproducible signal (e.p. potential) and does not require graphical interpretation. Titration with potentiometric detection may be performed automatically with the instrument previously described[11].

A number of titrations were made to a visual starch-iodine end-point. Although fairly satisfactory (error ± 0.5%) with macro amounts of antimony (8 mg) the precision of visual indication is much poorer than the electrometric detection techniques with small quantities of antimony.

ACKNOWLEDGEMENT

Appreciation is expressed to the Mallinckrodt Chemical Works for partial financial support of this study.

SUMMARY

A method is described for the coulometric titration of tripositive antimony with electrogenerated iodine, in a buffered solution of pH 8. The end-point can be detected either amperometrically, potentiometrically, or (less precisely) visually with starch indicator. Quantities of antimony between 0.06 and 10 mg are titratable with an average error of 0.001 to 0.01 mg.

RÉSUMÉ

Une méthode est décrite pour le dosage coulométrique de l'antimoine(III) au moyen de l'iode formé au cours du titrage, en solution tampon de pH 8. Le point final peut être déterminé soit ampérométriquement, soit potentiométriquement ou (de façon moins précise) visuellement avec l'amidon comme indicateur. Des quantités d'antimoine comprises entre 0.06 et 10 mg peuvent être titrées avec une erreur moyenne de 0.001 à 0.01 mg.

ZUSAMMENFASSUNG

Eine Methode zur coulometrischen Bestimmung von dreiwertigem Antimon mit elektrisch gebildetem Jod in einer Pufferlösung von pH 8 wird beschrieben. Der Endpunkt kann amperometrisch, potentiometrisch oder (weniger genau) optisch mit Stärke als Indikator bestimmt werden. Antimonmengen von 0.06 bis 10 mg können mit einem mittleren Fehler von 0.001 bis 0.01 mg titriert werden.

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A TITRATION OF A STRONG TRIBASIC ACID WITH A STRONG TRIACIDIC BASE

by

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That the hexamminocobalti and triethylenediaminocobalti hydroxides are strong bases has been recognized for some time[1,2]. An early attempt on our part to determine the basic dissociation constants of the hexammine hydroxide failed owing to some decomposition which occurred during its synthesis from the chloride and freshly prepared silver oxide or from the sulfate and barium hydroxide. The advent of strong base anion exchangers now makes it possible to prepare these hydroxides readily and in pure form.

That hexacyanocobaltic acid is a strong tribasic acid has been long known[3,4]. This acid can now be conveniently prepared on a strong acid cation exchanger[5], but it is necessary to exclude light to avoid photochemical decomposition of the acid.

We have now found by potentiometric titration that all three hydroxyl groups of hexamminocobalti and triethylenediaminecobalti hydroxides are strong bases and that all three hydrogen atoms of hexacyanocobaltic acid are strong acids. Hexacyanocobaltic acid was titrated directly with hexamminocobalti hydroxide and with triethylenediaminocobalti hydroxide. The potentiometric titration curves obtained are identical with those of a strong acid titrated with a strong base (Fig. 1). We believe that this is the first titration reported of a strong triacidic base with a strong tribasic acid.

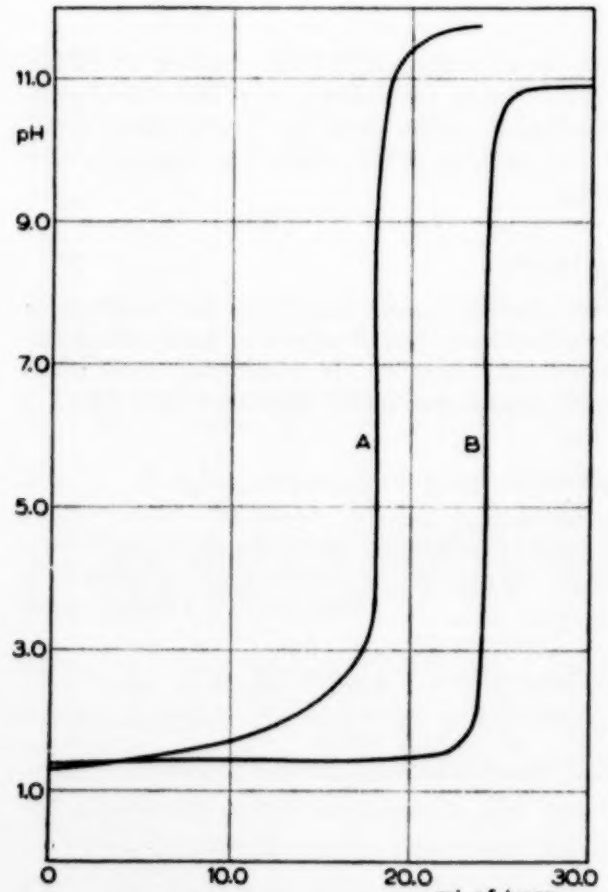

Fig. 1. Titration of hexacyanocobaltic acid with hexamminocobalti hydroxide (B) and with triethylenediaminocobalti hydroxide (A).

EXPERIMENTAL

Hexamminocobalti hydroxide was prepared by passing a solution of a weighed quantity of hexamminocobalti chloride dissolved in about 100 ml of water through a column of Amberlite IR-410 in the basic form. The column was well washed with water and the eluate was diluted to exactly 500 ml. The solution was stored in a polyethylene bottle. The hexamminocobalti hydroxide was standardized by titration with hydrochloric acid and it was then used to titrate hexacyanocobaltic acid. The results are shown in **Table** I. On standing the hexamminocobalti hydroxide decomposed to give some ammonia and cobalt hydroxide.

Triethylenediaminocobalti hydroxide was prepared by passing a weighed quantity of triethylenediaminocobalti bromide in about 100 ml of water through a column of Amberlite IR-410 in the basic form. The column was well washed with water and the eluate was diluted to exactly 500 ml. The solution was stored in a polyethylene bottle. This solution was standardized by titration with standard hydrochloric acid and it was then used to titrate hexacyanocobaltic acid.

Hexacyanocobaltic acid was prepared by passing a weighed amount of potassium hexacyanocobaltate in about 100 ml of water through a column of Amberlite IR-120 in the acid form, this operation being carried out in a dim light. The column was well washed and the eluate diluted to exactly 500 ml. The solution was stored in a dark bottle. The acid was standardized by titration with standard potassium hydroxide and it was then titrated with hexamminocobalti and with triethylenediaminocobalti hydroxides, the titration being performed in a dim light. The results are summarized in Table I; typical titration curves are shown in Fig. 1.

TABLE I

TITRATIONS OF HEXACYANOCOBALTIC ACID, HEXAMMINOCOBALTI HYDROXIDE AND TRIETHYLENEDIAMINOCOBALTI HYDROXIDE

Starting material	*Amount taken* g	*Titrated with*	*Normality* calculated	*Normality* found	*Per cent conversion to base (or acid)*
$[Co(NH_3)_6]Cl_3$	7.9740	HCl (0.0993*N*)	0.1790	0.1783	99.6
$[Co(en)_3]Br_3$	7.3784	HCl (0.0993*N*)	0.0925	0.0919	99.4
$K_3[Co(CN)_6]$	3.6622	KOH (0.0993*N*)	0.0682	0.0670	98.2
$K_3[Co(CN)_6]$	9.3975	KOH (0.0993*N*)	0.1750	0.1737	99.2
$H_3[Co(CN)_6]$	25.0 ml	$[Co(NH_3)_6](OH)_3$ (0.1783*N*)	0.1737	0.1726	
$H_3[Co(CN)_6]$	25.0 ml	$[Co(en)_3](OH)_3$ (0.0919*N*)			

SUMMARY

Hexacyanocobaltic acid, $H_3[Co(CN)_6]$, a strong tribasic acid, has been titrated potentiometrically with hexamminocobalti hydroxide, $[Co(NH_3)_6](OH)_3$, and with triethylenediaminocobalti hydroxide, $[Co(en)_3](OH)_3$, both strong triacidic bases.

RÉSUMÉ

L'acide hexacyanocobaltique, $H_3[Co(CN)_6]$, acide tribasique fort, peut être titré potentiométriquement avec l'hydroxyde d'hexamminocobalt(III), $[Co(NH_3)_6](OH)_3$, et avec l'hydroxyde de triéthylènediaminocobalt(III), $[Co(en)_3](OH)_3$, tous deux des bases trivalentes fortes.

ZUSAMMENFASSUNG

Die Hexacyanocobaltisäure, $H_3[Co(CN)_6]$, eine starke dreibasische Säure, wurde potentiometrisch mit Hexamminocobaltihydroxyd, $[Co(NH_3)_6](OH)_3$, und mit Triäthylendiaminocobaltihydroxyd, $[Co(en)_3](OH)_3$, die beide starke dreiwertige Basen sind, titriert.

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DIE BESTIMMUNG DES SAUERSTOFFGEHALTES VON KESSELSPEISEWASSER

von

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EINLEITUNG

Genügte noch vor einigen Jahrzehnten die klassische Winklermethode zur Sauerstoffbestimmung in Kesselspeisewasser, so hat die Entwicklung des Kesselbetriebes die Anforderungen auch in dieser Hinsicht beträchtlich verschärft, sodass man heute einen Sauerstoffgehalt von einigen Tausendsteln mg pro Liter mit genügender Genauigkeit bestimmen können soll. Die sehr niedrigen Sauerstoffgehalte des Speisewassers für Hochdruckkessel erfordern eine Bestimmungsmethode die eine Genauigkeit von zumindest 1 γ/l aufweist und trotzdem zur Betriebsanalyse geeignet ist.

Man hat versucht, die Messgenauigkeit der Winklermethode zu verbessern und deren Fehler, die durch die Anwesenheit von Sauerstoff in den Reagenzien und durch die oxydierenden und reduzierenden Substanzen im Wasser verursacht werden, zu beseitigen.

Im Laufe der Zeit sind mehr als 25 Änderungen der Winklermethode sowie neue Bestimmungsweisen vorgeschlagen worden.

Wir haben einige der wichtigsten Methoden einer Prüfung unterzogen und eine von diesen als die zweckmässigste befunden, welche nun seit 1951 in den niederländischen elektrischen Kraftwerken benutzt wird. Über diese Methode und die Erfahrungen damit wird in dieser Publikation berichtet.

VERGLEICH DER WICHTIGSTEN METHODEN

Die Messgenauigkeit folgender Methoden wurde verglichen:

1. *Die klassische Winklermethode*

2. *Die Ferromethode von Wickert*[1]

Der Sauerstoff oxydiert eine in der Probe erzeugte Ferrohydroxydfällung. Das gebildete Ferrihydroxyd wird kolorimetrisch mit Rhodanid bestimmt. Etwa schon vorhandenes Ferri wird berücksichtigt.

3. *Die Tolidinmethode*

Diese Methode von McCrumb und Kenny[2] wurde von Zimmermann für Kesselspeisewasser eingeführt[3]. Ein Tolidinzusatz ergibt mit dem mehrwertigen Mangan

Literatur S. 284

ein Farbkomplex, das kolorimetrisch gemessen wird. Von WICKERT[4] wurde eine Korrektion für den Ferrogehalt des Wassers vorgeschlagen.
FREIER[5] bestimmt den Gehalt an reduzierenden Substanzen mit einer O_2-Standardlösung und korrigiert für den in den Reagenzien gelösten Sauerstoff.
WICKERT UND IPACH[6] oxydierten die reduzierenden Substanzen vorher mit Brom.
SCHUMANN[7] gibt eine Änderung der Tolidinmethode indem er mit Certrichlorid statt mit Mangandichlorid arbeitet und sofort beim Ansäuern das Tolidin hinzufügt.

4. *U.S. Navy Laboratorium-Methode*[8] *(potentiometrische Titration)*

Zur Beseitigung der Störungen wird neben der eigentlichen Bestimmung ein Blindversuch durchgeführt, wobei die Schwefelsäure vor dem Mangansulfat zugesetzt wird. Die jodidhaltige Lauge wird mit etwas Jod versetzt, damit alle Reaktionen mit den im Wasser anwesenden reduzierenden Substanzen sich mit einem Jodüberschuss abspielen.
Die beiden Proben der Bestimmung und des Blindversuchs werden potentiometrisch titriert. Für den Sauerstoff in den Reagenzien wird ein fester Betrag subtrahiert.

5. *"Dead-stop-end-point"-Methode*

Statt potentiometrisch werden die Endlösungen nach dem dead-stop-end-point-Verfahren titriert. Dieses Polarisations-Verfahren wurde von FOULK UND BAWDEN[9] veröffentlicht und von ULMER, REYNAR UND DECKER[10] für Kesselspeisewasser angewendet. Wir haben diese Methode unter Berücksichtigung einiger später angeführter Abänderungen verwendet.

Die mit Speisewasser und Kondensaten im Betrieb und die mit entgastem destilliertem Wasser im Laboratorium erhaltenen Untersuchungsergebnisse sind in Tafel I eingetragen.

Es erweist sich, dass bei der ganzen Manipulationsreihe wie ursprünglich von WINKLER angegeben, die Gesamtgenauigkeit — ungeachtet Einfluss und Beseitigung der Störungen — durch die Genauigkeit bestimmt wird, womit der Endpunkt der Endtitration festgestellt werden kann. Die potentiometrische Titration und die d.s.e.p.-Titration besitzen die grösste Messempfindlichkeit und -genauigkeit. Sie zeigten sich für unser Ziel daher am geeignetsten.

Die potentiometrische Titration hat den Nachteil dass sie ziemlich viel Zeit in Beschlag nimmt, weil die Einstellzeit der Spannung in der Nähe des Umschlagpunktes etwa vier bis sechs Minuten beträgt. Wohl konnten wir feststellen, dass der Wendepunkt in der Spannungskurve sich nicht ändert wenn die Spannung, unter genau eingehaltenen Bedingungen für Titrations-, Warte- und Rührzeiten, bei der Titration gemessen wird ehe sie konstant geworden ist; die gesamte Titrationszeit bleibt aber länger als bei der d.s.e.p.-Methode. Die d.s.e.p.-Methode hat sich daher auch als Betriebsmethode am Besten bewährt[13].

Im Folgenden wird über einige wichtige Einzelheiten, auf die wir während unserer Untersuchungen gestossen sind sowie über den Einfluss einiger Störstoffe bei dieser Methode berichtet.

Literatur S. 284

TAFEL I

SAUERSTOFFGEHALT IN γ/l NACH VERSCHIEDENEN METHODEN

Methode	*Winkler*	*Ferro*	*Tolidin*	*Tolidin Rhodanid*	*U.S.Navy pot. Titr.*	*d.s.e.p.*
Analysen-zahlen	0	0			0.13	0.2
	0	0			1.02	0.9
		4				2.9
			0	5		3.1[a]
			0	3		3.3[a]
	0	4			5.11	5.3
	0		0	8		6.3[a]
		3			6.82	6.4
	0	6			7.74	8.0
					11.0	10.8
			8	16		14.4[a]
			15	25		19.8[a]
			28	28		21.0
			15	37		40.0[a]
	60	62				54.3
			65	65		60.6
	170	106				100
	160	106				101
			96	96		103
					108	109
		149				145
			140	140		188
	250	161				197
	310	254			203	204
	600	270				594
Empfindlichkeit in γ/l	20[b]	2 bis 3	2 bis 3	2	0.06[c]	0.4

[a] Das Wasser enthält Ferrosalze in kleiner Konzentration.

[b] Später ist von FREIER[11] und von PIETERS[12] die Messung des Stärkeumschlages verschärft. Die Messgenauigkeit der d.s.e.p.-Methode wird aber nicht erreicht.

[c] Angabe der Literatur[10].

D.S.E.P.-METHODE

Aus Fig. 1 ist die elektrische Schaltung ersichtlich, welche bei der d.s.e.p.-Methode angewendet wurde. Mittels einer Taschenbatterie und eines Spannungsteilers wird an die Titrierzelle, die aus zwei im Titriergefäss eingetauchten Platinelektroden besteht, eine Spannung von etwa 150 mV angelegt. Das Abfallen der Spannung durch Depolarisation am Schluss der Titration wird mit einem Röhrenmillivoltmesser festgestellt. Es ist auch möglich, die Titrierzelle an das Gitter einer Triode anzuschliessen, die einen Zweig einer einfachen Brückenschaltung bildet (Fig. 2).

Wir konnten feststellen, dass bei dieser Ausführungsweise folgendes zu beachten ist.

1. Platinelektroden

Die Platinelektroden werden in solcher Weise in ein gläsernes Rohr eingeschmolzen, dass sich der gepunktschweisste Übergang von Elektrode auf Zuleitungsdraht inner-

Literatur S. 284

halb des Rohres befindet. Ohne diese Massnahme würden Spuren metallischen Kupfers vom Punktschweissen zur völligen Zerstörung der Elektrodenpolarisation bei der Bestimmung führen.

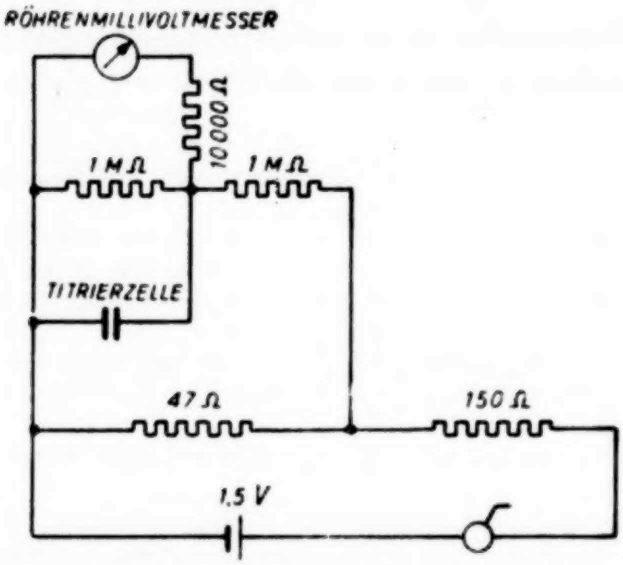

Fig. 1. Elektrische Schaltung bei der d.s.e.p.-Methode.

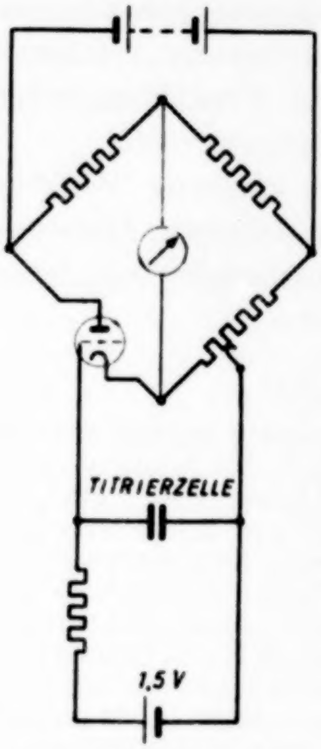

Fig. 2. Modifizierte Schaltung bei der d.s.e.p.-Methode.

Ferner ist es nötig, iridiumfreies Platin zu verwenden, weil Iridium die Polarisationsspannung des Platins erniedrigt.

2. *Sauerstoff in den Reagenzien*

Wir verwendeten die von ADAMS *c.s.* vorgeschlagene Korrektion für den Sauerstoff in den Reagenzien, wobei diese einige Tage an der Luft stehen gelassen werden und dann ein konstanter Fehler in Rechnung gebracht wird, der für eine Probe von 500 ml 0.0104 mg/l beträgt. Für die übrigen Berichtigungen genügen dann zwei Proben.

3. *KOH/KJ/J_2-Lösung; Jodverbrauch des Wassers*

Beim Lösen des Jods in der KOH/KJ-Lösung treten zwei Reaktionen auf[14]:

$$J_2 + 2\,OH^- \rightleftarrows JO^- + J^- + H_2O \quad \text{(1)}$$

$$3\,JO^- \rightarrow JO_3^- + 2\,J^- \quad \text{(2)}$$

von welchen (1) rasch und (2) langsam verläuft.

In der Annahme, dass auch (2) ein Gleichgewicht ist, liegt eine Erklärung für einige Unbequemlichkeiten, die leicht aufgehoben werden können.

So ist es nötig, das Reagenz unter einem Glasstöpsel aufzubewahren, weil ein Gummistöpsel — womit die Flasche sich leichter öffnen liesse — wegen der auch in stark alkalischer Lösung noch immer anwesenden kleinen Jodpartialspannung nach einigen Tagen das Jod gänzlich aus der Lösung aufnimmt.

Literatur S. 284

Die Umsetzung von Hypojodit in Jodat spielt wahrscheinlich eine Rolle bei der Blindwertänderung in frisch bereitetem Reagenz, das daher vor Gebrauch einige Tage stehen gelassen werden soll. Jedenfalls ist auch das Wasser, das zur Herstellung des Reagenzes gebraucht wird, von Einfluss, weil die Grösse der Blindwertänderung sich als von der Wasserart abhängig erwies. Offenbar können sich im Wasser organische Verunreinigungen befinden, die nur langsam von Hypojodit bzw. Jodat angegriffen werden.

Diese langsame Reaktion von gewissen organischen Verbindungen mit Jod erfordert auch beim Blindversuch eine Wartezeit von 15 Minuten nach Hinzufügen des Reagenzes, falls viele derartige Verbindungen vorhanden sind.

Arbeitsweise

Gleichzeitig werden zwei Proben genommen, wovon eine zur Ermittlung des Blindwertes dienen soll. Die Probe zur eigentlichen Sauerstoffbestimmung wird nacheinander mit 2 ml KOH/KJ/J_2-Lösung, 2 ml $MnSO_4$-Lösung und nach Umschwenken und einer Viertelstunde Wartezeit noch mit 2 ml Schwefelsäure versetzt. Die Blindprobe wird nach Zugabe der KOH/KJ/J_2-Lösung zuerst mit Schwefelsäure und danach mit der $MnSO_4$-Lösung versetzt. In Wasser mit vielen oxydierbaren Stoffen empfiehlt es sich, auch diese Blindprobe nach Zugabe der KOH/KJ/J_2-Lösung eine Viertelstunde stehenzulassen.

Die KOH/KJ/J_2-Lösung soll sehr genau abgemessen werden und zwar mit einer Spezialpipette, die innerhalb 0.001 ml geeicht ist.

Nach Auflösen des Manganniederschlages wird die Lösung in die Titrierzelle gebracht und mit 1 ml 0.005*N* Thiosulfat versetzt. Auch diese Menge soll sehr genau abgemessen werden. Nach Einschalten des Messgerätes soll dieses eine Spannung von 100-150 mV anzeigen. Ist dies nicht der Fall, so wird nochmals, ebenfalls mittels einer Spezialpipette, 1 ml 0.005*N* Thiosulfat zugegeben. Jetzt wird mit 0.005*N* KJO_3 unter konstanter Rührgeschwindigkeit titriert. Die Näherung des Umschlagpunktes kündigt sich meistens durch eine kleine Spannungssteigung von etwa 5 mV an. Sobald die Spannung zurückgeht schliesst man den Büretthahn.

Unterdessen soll man dauernd gleichmässig rühren. Man überzeuge sich ob die Spannung wirklich ohne weitere Thiosulfatzugabe in nicht zu langer Zeit auf höchstens die Hälfte des ursprünglichen Wertes zurückgeht; dies wird fast immer der Fall sein. Die Titration ist dann beendet.

Der Sauerstoffgehalt wird berechnet aus

$$S = [(a_1 - b_1)\, t_1 - (a_2 - b_2)\, t_2 - 0.00064]\, \frac{8}{V-4}$$

worin S = Sauerstoffgehalt in γ/l
a_1 = ml Thiosulfat bei der Hauptprobe
b_1 = ml Thiosulfat beim Blindversuch
t_1 = Titer der Thiosulfatlösung
a_2 = ml KJO_3 bei der Hauptprobe
b_2 = ml KJO_3 beim Blindversuch
t_2 = Titer der Kaliumjodatlösung
0.00064 = Korrektion für in den Reagenzien gelösten Sauerstoff
V = Volumen der Probeflasche.

STÖRUNGEN BEI DER D.S.E.P.-METHODE

Bei der Anwendung der Methode im Betrieb wurden verschiedene Störungen empfunden, die eine nähere Laboratoriumuntersuchung notwendig machten.

Sehr reines, fast sauerstoffreies Wasser wurde durch aufeinander folgende thermische Entgasung, chemische Bindung des Sauerstoffs mittels Natriumsulfit und Vollentsalzung erhalten. Auch wurde eine gute Entgasung erreicht wenn das Wasser über einen stark basischen mit Sulfit beladenen Austauscher geführt wurde. Das Leitvermögen des ablaufenden Wassers zeigte den theoretischen Wert von 0.05 μS, der Sauerstoffgehalt war oft weniger als 1 γ/l.

Literatur S. 284

Die etwaigen Störungen durch Kupfer- und Eisensalze, Nitrat und Nitrit, Sulfit und Hydrazin, wurden untersucht.

Bei der Untersuchung wurden vier Proben genommen. Zwei Proben dienten zur Sauerstoffbestimmung des Wassers. Zu den anderen zwei Proben wurde eine bekannte Menge luftgesättigten Wassers, das die störende Substanz enthielt, hinzugefügt. Die dabei zugefügten Sauerstoffmengen wurden aus der Löslichkeit errechnet.

1. Ohne störende Substanzen

Zur Prüfung der Annahme, dass die anwesende Sauerstoffmenge einfach aus Löslichkeitstafeln berechnet werden kann, wurde eine Probereihe ohne Störstoffe untersucht.

Die Ergebnisse sind in Tafel II angegeben.

TAFEL II

SAUERSTOFFGEHALTE γ/l

berechnet	*gefunden*
1.2	1.3
1.4	1.4
2.0	2.3
3.0	3.2
6.2	6.3
11.5	11.9
19.4	19.2
34.7	35.8
80.8	82.3

2. Kupfer

Kupri- sowie Kuprosulfat wurden in Mengen bis 1 mg/l zugesetzt. Störungen wurden nicht beobachtet. Auch der Blindwert änderte sich nicht.

Wie aus den beim Punktschweissen der Platinelektroden begegneten Schwierigkeiten begreiflich ist, traten Unregelmässigkeiten auf, die wahrscheinlich durch eine winzige Kupferabscheidung an den Titrierelektroden verursacht wurden. Da die Polarisation zweifellos eintritt bevor Kupfer abgeschieden werden kann, wurde sie auch nicht ganz verhindert, sondern äusserte sich die Störung nur in einer langsameren Einstellung der Spannung auf einen niedrigeren Wert.

3. Eisen

Sowohl die Störung von Ferri- als von Ferroionen wurde bis zu Gehalten von 3 mg pro Liter untersucht.

Die Polarisationsspannung stellte sich bei eisenhaltigen Lösungen bei einem Gehalt über 0.3 mg pro Liter noch langsamer ein als in kupferhaltigen Lösungen und erreichte nur einen Wert von 70 mV.

Bei Anwesenheit von Ferri- oder Ferroionen wird bei Gehalten die höher sind als 0.1 mg pro Liter zu viel bzw. zu wenig Sauerstoff gefunden.

Der Blindwert ändert sich bei Ferriionen nicht, wohl aber bei Ferroionen über 0.1 mg/l. Es wird mehr Jodat verbraucht.

Offenbar tritt bei der Bestimmung bei Anwesenheit von Ferriionen eine Reduktion des Ferrieisens auf: $Fe^{+3} + Mn^{+2} \rightarrow Fe^{+2} + Mn^{+3}$. Die Reaktion verläuft aber

Literatur S. 284

während der Bestimmung nicht quantitativ, denn die zuviel gefundene Sauerstoffmenge war immer niedriger als mit der Ferrimenge übereinstimmte.

Bei Anwesenheit von Ferroionen findet eine Oxydation von Ferroeisen statt, sowohl bei der Bestimmung wie auch beim Blindversuch. Auch hier aber geht die Reaktion nicht vollständig vor sich. Es ist möglich, den prozentualen Umsatz von Ferro in Ferri aus den Analysenzahlen zu berechnen. Es zeigte sich z.B. dass bei 1 mg/l Ferro beim Blindversuch 54% und bei der Bestimmung 66% Ferro oxydiert worden war.

Die Störungsreaktion verläuft also sowohl beim Blanko als bei der Bestimmung nicht quantitativ, offenbar wegen der niedrigen Eisenkonzentrationen.

Es war nicht möglich, die Störung durch Bildung von Komplexen mit Natriumpyrophosphat, Weinsäure, Kaliumtartrat oder Natriumfluorid völlig zu beseitigen. Vielleicht ist die Reaktionszeit zur Komplexbildung bei diesen niedrigen Eisenkonzentrationen zu gross.

Unter 0.1 mg/l wurden bei Ferro- wie bei Ferrieisen richtige Werte erhalten. Offenbar ist die Geschwindigkeit der Störungsreaktion bei diesen niedrigen Eisenkonzentrationen so gering, dass diese bei der Sauerstoffbestimmung nicht mehr stören.

4. *Nitrat und Nitrit*

Bei Anwesenheit von Nitrat bis 100 mg pro Liter wurde keine Störung beobachtet. Auch der Blindwert ändert sich nicht.

Bei Anwesenheit von Nitrit wurde, sowohl beim Blindversuch als bei der Bestimmung, Jod vom Nitrit freigemacht.

$$2\,HNO_2 + 2\,HJ \rightarrow J_2 + 2\,H_2O + 2\,NO.$$

Bei der Bestimmung kommt mehr Jod frei als beim Blindversuch. Aus den Analysenzahlen lässt sich die freigemachte Jodmenge berechnen (Tafel III).

TAFEL III

NITRITSTÖRUNG

Menge NO_2^- m.Äq/l	*Freigemachtes Jod m.Äq/l*	
	Blindwert	*Bestimmung*
0.0013	0.0013	0.0013
0.0026	0.0019	0.0021
0.0039	0.0023	0.0028
0.0065	0.0032	0.0086

Bei niedrigen NO_2^--Gehalten (bis 0.1 mg NO_2^-/l) findet also noch keine Störung statt und kann die d.s.e.p.-Methode ohne weiteres benutzt werden. Bei höheren Konzentrationen kann die Störung durch einen Natriumazidzusatz völlig beseitigt werden. Bei 10 mg NO_2^-/l müsste 100 mg Natriumazid zugesetzt werden.

5. *Hydrazin*

Hydrazin wurde bei Konzentrationen bis 100 γ/l untersucht. Höhere Hydrazinkonzentrationen werden in der Praxis nicht vorkommen. Eine Störung wurde nicht beobachtet. Auch der Blindwert änderte sich nicht.

Literatur S. 284

Dieser Befund scheint in erster Ansicht unbegreiflich, weil ja Hydrazin mit Jod bestimmt werden kann[15]. Die Reaktion des Hydrazins mit Jod verläuft jedoch in der sauren Mitte der End-Titration äusserst träge. In der alkalischen Lösung ist das Jod während der Bestimmung als Jodat anwesend, das offenbar nicht von Hydrazin angegriffen wird.

6. *Sulfit*

Sulfit stört nicht wenn nur mit der KOH/KJ/J_2-Lösung genügend Jod hinzugefügt wird um das Sulfit völlig zu binden. Ohne das kann man sogar negative Sauerstoffgehalte erhalten[16]. Man soll also nachprüfen, ob nicht schon vor der endgültigen Thiosulfatzugabe Polarisation eintritt, die von einem noch vorhandenen Sulfitrest herrühren würde.

VERMEIDUNG DER STÖRUNGEN

Im Vorgehenden wurde gezeigt, dass es nicht immer möglich ist die Störungen durch Zugabe bestimmter Chemikalien völlig zu beseitigen.

Es ist daher am Besten, die störenden Substanzen vorher aus dem Wasser zu entfernen. Dies ist mit Ionenaustauschern möglich. In die Probeleitung wird ein Filter eingeschaltet, welches mit einer Mischung von H– und OH–Austauschern gefüllt ist. Die anorganischen Substanzen werden völlig entfernt, während die organischen Substanzen bei richtiger Wahl der Austauscher auf einen sehr niedrigen Gehalt zurückgebracht werden können.

Die Austauscher beeinflussen die Sauerstoffbestimmung nicht, wie die in Tafel IV gesammelten Ergebnisse mit verschiedenen Austauschern an einem Turbinenkondensat zeigen.

TAFEL IV

Probe	*Sauerstoff* γ/l
Turbinenkondensat	50.5
Nach Dusarit*	50.2
Nach Amberlite IR 120	50.0
Nach Amberlite IRA 400	50.5
Nach Amberlite IRA 401	50.7
Nach Amberlite IRA 410	50.8
Nach Amberlite IRA 411	49.9
Nach IMACA 17*	50.7

* Diese Austauscher auf Kohlebasis erhöhen nicht nur den Blindwert sondern in gleichem Masse auch den Bestimmungswert, sodass trotzdem der richtige Sauerstoffgehalt gefunden wird.

ZUSAMMENFASSUNG

Es wird gezeigt, dass die "dead-stop-end-point"-Methode und die potentiometrische Titration zur Sauerstoffbestimmung in Kesselspeisewasser die grösste Messgenauigkeit und Empfindlichkeit besitzen.

Mit der d.s.e.p.-Methode arbeitet man schneller. Diese hat sich daher als Betriebsmethode bewährt. Ihre Genauigkeit von 0.4 γ/l genügt der Praxis. Zur Verarbeitung der Proben wurde nach der U.S. Navy-Methode verfahren. Hierbei können Störungen von den im Wasser anwesenden organischen und anorganischen reduzierenden und oxydierenden Substanzen auftreten.

Das Ausmass der Störung wurde für Kupfer, Eisen, Nitrat und Nitrit, sowie Hydrazin und Sulfit untersucht. Kupfer, Nitrat, Hydrazin und Sulfit stören beim beschriebenen Analysengang nicht. Es wird beschrieben, wie die Störungen vermieden werden können.

Literatur S. 284

SUMMARY

The high precision and sensibility of the dead-stop-end-point and potentiometric titration methods make them very suitable for the oxygen determination in boiler feed water. The d.s.e.p. method requires less time. Hence this method has been adapted for use in boiler plants. Its accuracy of 0.4 γ/l is sufficient for the purpose.

For the treatment of the samples the U.S.Navy method was followed. Disturbances may be caused by organic and inorganic reducing and oxidizing agents present in the water.

The degree of disturbance has been examined for copper, iron, nitrate and nitrite, hydrazine and sulfite. Copper, nitrate, hydrazine and sulfite do not cause errors.

A description is given of how the disturbances can be avoided.

RÉSUMÉ

Les dosages par potentiométrie et par la méthode du "dead-stop-end-point" sont très sensibles et précis et conviennent donc au dosage de l'oxygène dans l'eau alimentaire des chaudières. La méthode du "dead-stop-end-point" est la plus rapide et elle est avantageuse pour une analyse technique, sa précision de 0.4 γ/l étant suffisante. Les échantillons à analyser sont traités selon la méthode de la "U.S. Navy". La présence de réducteurs ou d'oxydants organiques et minéraux dans l'eau gêne le dosage. L'influence du cuivre, du fer, de l'hydrazine, des anions nitriques, nitreux et sulfureux est examinée. Le cuivre, l'hydrazine et les ions nitriques et sulfureux ne gènent pas. Il est possible de supprimer l'influence des ions perturbateurs.

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ÉTUDE DE DIFFÉRENTS MODES DE TRACÉS ET D'ENREGISTREMENT DES COURBES DE POLARISATION

par

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De nombreux ouvrages[1,2,3,4] fournissent tous les renseignements relatifs aux montages électriques manuels et enregistreurs permettant d'obtenir les courbes de polarisation. Ces courbes traduisent les variations de l'intensité d'électrolyse en fonction du potentiel de l'électrode considérée. Les systèmes enregistreurs utilisés ont en général une particularité commune: l'intensité d'électrolyse est enregistrée en fonction du temps, tandis que la tension appliquée aux bornes de la cellule varie linéairement en fonction du temps. Il se pose alors deux questions: (I) Cette tension est-elle toujours proportionnelle au potentiel de l'électrode étudiée? (II) La vitesse avec laquelle varie cette tension est-elle suffisamment réduite pour que l'on atteigne un état d'équilibre (compte tenu d'une agitation constante de la solution, d'un renouvellement de la surface de l'électrode, ou d'une rotation à vitesse constante de l'électrode)? Ce sont ces deux points que nous allons essayer de préciser successivement.

I. CONDITIONS DE PROPORTIONNALITÉ ENTRE LA TENSION APPLIQUÉE ET LE POTENTIEL DE L'ÉLECTRODE

1. Relation entre les différentes grandeurs du circuit électrique

Soit une cellule constituée de deux électrodes A et B, plongeant dans une solution conductrice. La résistance entre A et B est r.

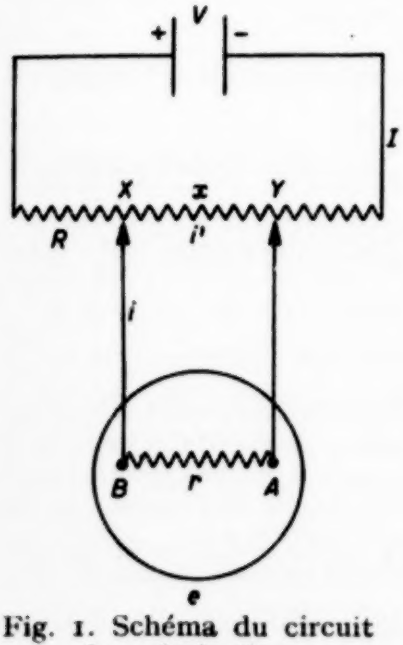

Fig. 1. Schéma du circuit de polarisation.

Pour simplifier les calculs et aussi parce que cela est généralement le cas, admettons que l'électrode B ait un potentiel indépendant de l'intensité d'électrolyse (électrode au calomel de grande surface). La force électromotrice ou contre-électromotrice de la cellule e sera donc égale au potentiel de l'électrode A par rapport à une électrode au calomel.

Considérons ensuite le circuit complet de polarisation. Soit V la source de tension constante, soit R la résistance totale du potentiomètre dans laquelle elle débite, soit x la résistance comprise entre les points X et Y reliés à la cellule, soit I l'intensité totale sortant de la source de tension, i l'intensité traversant la cellule et i' celle qui traverse la résistance x (Fig. 1). La relation existant entre les grandeurs i, e, x, R, r, V, est établie en appliquant les lois de Kirchoff aux différentes mailles, soit:

$$e = \frac{V}{R}\, x - i \cdot r - i \cdot \frac{x}{R} \cdot (R - |x|) \qquad (1)$$

Les conventions de signes sont les suivantes:

$i > 0$ lorsqu'à l'électrode A se produit une oxydation.
$e > 0$ si le potentiel de l'électrode A est supérieur à celui de l'électrode B.
$x > 0$ si l'électrode A (point Y) est reliée au pôle + de la source de tension.

2. *Enregistrement des courbes $i = f(e)$*

Comme nous l'avons dit, la solution la plus couramment utilisée, consiste à enregistrer la courbe d'intensité d'électrolyse en fonction du temps et à supposer que le potentiel de l'électrode varie linéairement en fonction de ce même paramètre temps.

Pratiquement, on dispose d'un potentiomètre R bobiné que l'on fait tourner à vitesse constante et d'une source de tension constante branchée aux bornes de ce potentiomètre. Il faut remarquer que la grandeur qui varie linéairement en fonction du temps est la fraction x de la résistance R et non pas le potentiel e.

D'après la relation (1) la grandeur e ne sera proportionnelle à x, donc au temps, que si les deux termes $i \cdot r$ et $i \cdot \frac{x}{R}(R - |x|)$ sont tous deux négligeables devant e.

Le terme $i \cdot r$ dépend de la cellule. La résistance r devient importante soit lorsqu'on utilise des ponts d'agar-agar pour éviter toute diffusion de certains ions du compartiment anodique au compartiment cathodique, soit lorsqu'on emploie des solvants autres que l'eau comme l'acide acétique anhydre.

Le terme $i \cdot \frac{x}{R}(R - |x|)$ dépend de la valeur de la résistance du potentiomètre utilisé. KOLTHOFF[1] indique qu'en polarographie il suffit de prendre $R < 100\ \Omega$ pour rendre ce terme négligeable. Ce terme devient important dans le cas où on utilise de fortes intensités de courant (électrogravimétrie ou coulométrie à potentiel contrôlé). Lorsque les deux termes précédents ne sont pas négligeables, nous proposons les trois solutions suivantes:

a. Enregistrer simultanément e et i en fonction de x (c'est-à-dire du temps) à l'aide d'un enregistreur à deux voies, soit $e = f(x)$ et $i = f(x)$.

b. Faire varier e linéairement en fonction du temps (t) à l'aide d'un potentiostat et enregistrer $i = f(t) = g(e)$.

c. Faire varier i linéairement en fonction du temps (t) à l'aide du même potentiostat monté différemment et enregistrer $e = f(t) = g(i)$.

Remarque

Deux groupes d'auteurs JACKSON ET ELVING[5] d'une part et NICHOLSON[6] d'autre part, viennent de proposer une autre solution; ces auteurs, après avoir mesuré avec précision la résistance r de la cellule, compensent automatiquement la chute ohmique $i \cdot r$ soit par un procédé électronique soit par un simple contre-courant tel que la force électromotrice appliquée aux bornes de la cellule soit égale à e. On peut remarquer que dans ces conditions le terme $i \cdot \frac{x}{R}(R - x)$ n'est pas corrigé.

Enfin ARTHUR, LEWIS ET LLOYD[7] ont proposé un système à trois électrodes mais nous n'avons trouvé dans la littérature qu'un résumé de leur travail.

Bibliographie p. 291

II. OBTENTION D'UN ÉTAT DE RÉGIME DANS LE CAS D'UNE SOLUTION AGITÉE A VITESSE CONSTANTE

Le potentiel de l'électrode étant fixé, l'intensité de courant est-elle constante et vice versa? Pour étudier ce phénomène nous avons opéré de la façon suivante: nous réalisons une variation régulière mais discontinue de l'une des trois grandeurs x, e, ou i, suivant le mode de polarisation utilisé. Considérons par exemple le cas de la variation régulière mais discontinue de e. L'enregistrement de l'intensité pendant les intervalles de temps (2 min) correspondant à un potentiel constant, permet d'observer si cette intensité est stable ou non. Nous reportons sur la Fig. 2 l'oxydation de l'ion I^- en milieu tampon monochloracétique. La vitesse de polarisation est telle que nous obtenons 3 pointés de l'intensité (toutes les 38 secondes) à chaque niveau de potentiel. Nous constatons que l'équilibre est atteint dans la région A B C de la courbe, ce qui correspond à l'oxydation de I^- et au palier de diffusion; en effet, les trois pointés successifs de i sont sur une horizontale. La partie D E correspondant à l'oxydation de l'eau indique que l'intensité décroît constamment pendant le temps où le potentiel est constant et qu'aucun état de régime n'est atteint. La partie C D correspond à un changement d'état de l'électrode (formation d'une couche d'oxyde comme l'ont montré **Kolthoff et Tanaka**[8]). Sur la même Fig. 2, nous reportons le polarogramme relatif à l'électrolyte support (tampon CH_2ClCO_2H). Nous retrouvons une stabilité des intensités de courant jusqu'au potentiel correspondant au changement d'état de l'électrode. Nous avons également réalisé le polarogramme

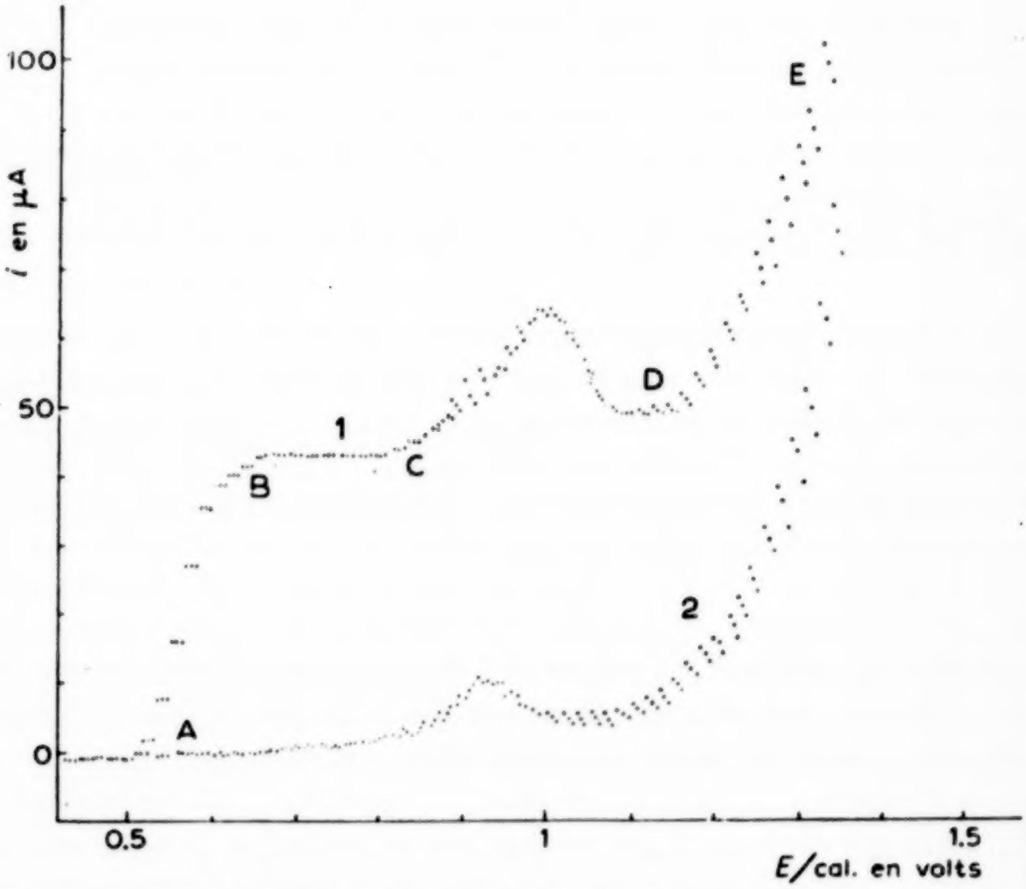

Fig. 2. Courbes de polarisation, mode de polarisation b.
1: Oxydation de I^- 0.003M;
2: Oxydation de l'électrolyte support: tampon monochloracétique 0.05M.

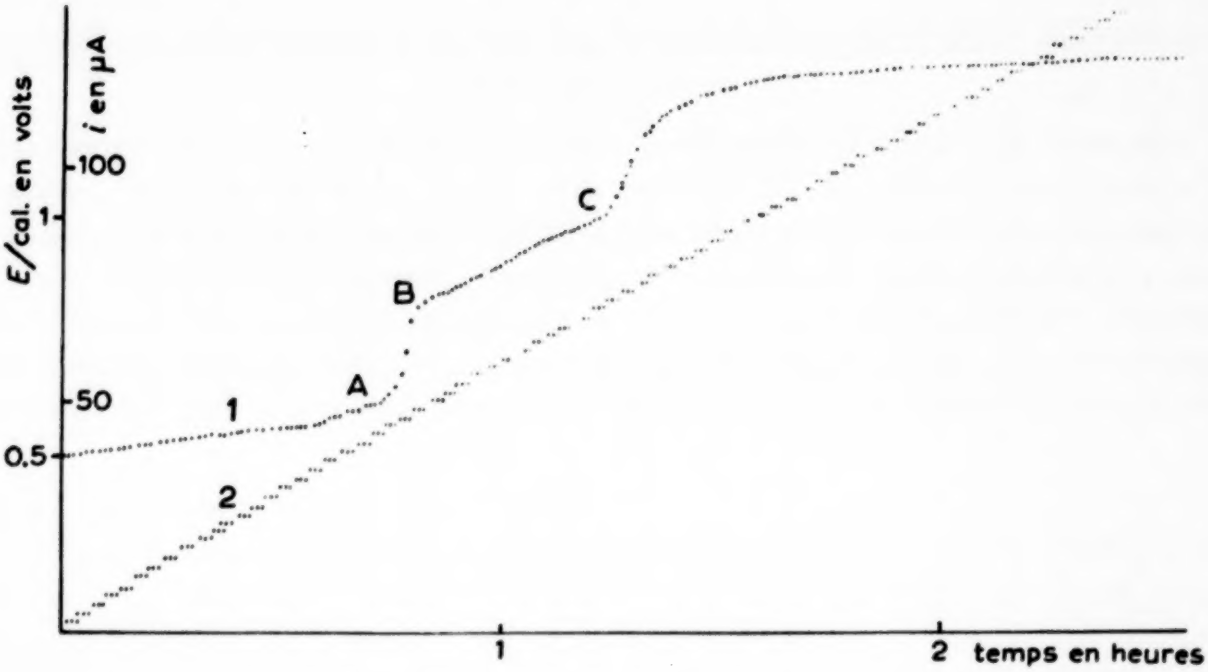

Fig. 3. Oxydation des ions I^- 0.003*M* dans un tampon monochloracétique 0.05*M*, mode de polarisation c. 1: $e = f(t)$; 2: $i = f(t)$.

de l'ion I^- en faisant varier linéairement l'intensité en fonction du temps (Fig. 3). Nous constatons au contraire une instabilité des potentiels dans la région A B: ceci montre que la vitesse de polarisation, dans ce cas, est trop rapide pour espérer obtenir un état de régime. (En effet les trois pointés successifs de potentiel sont constamment croissants et non situés sur une horizontale.) Le changement d'état de l'électrode correspond ici au palier incliné B C.

Remarques

1) Les courbes de polarisation relatives à l'oxydation des ions I^- tracées par les modes b et c ne sont pas superposables puisque l'état de régime n'est pas atteint dans les mêmes parties du domaine intensité-potentiel (voir Fig. 4).

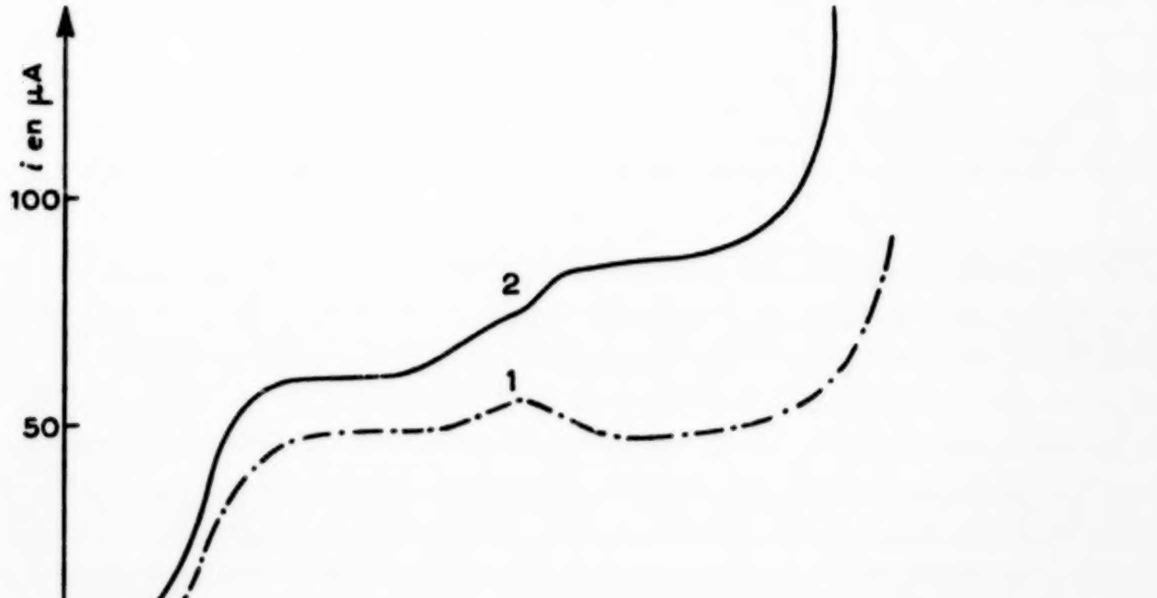

Fig. 4. Oxydation des ions I^- 0.003*M* dans un tampon monochloracétique 0.05*M*. 1: mode de polarisation b; 2: mode de polarisation c.

Bibliographie p. 291

2) La variation linéaire de l'intensité en fonction du temps et l'enregistrement du potentiel de l'électrode (mode c) nous parait être le mode de polarisation le plus adapté à la détermination du domaine de potentiel ou se produit un changement d'état de l'électrode.

Le tracé discontinu des courbes de polarisation permet ainsi de préciser la région du domaine intensité-potentiel où l'état de régime est atteint.

III. DESCRIPTION DES DISPOSITIFS EXPÉRIMENTAUX

1. Cellule d'électrolyse

La solution contenue dans le récipient est agitée par un agitateur magnétique. L'électrode de platine polie (électrode *A*) plongeant dans la solution est constituée par un fil de 1 cm de long et 1 mm de diamètre: deux électrodes au calomel sont reliées à la solution par l'intermédiaire de ponts d'agar-agar au nitrate de potassium. L'une de ces électrodes (électrode *B*) permet de fermer le circuit d'électrolyse, l'autre (éléctrode *C*) permet d'atteindre le potentiel de l'électrode de platine *A* et sert d'électrode de référence.

2. Dispositif polariseur

α. Dispositif simple. Mode de polarisation a

Une source de tension constante est appliquée aux bornes d'un potentiomètre calibré (85 Ω) entraîné par un moteur synchrone. La source de tension est constituée par un élément de 2 volts d'une batterie d'accus. La vitesse de rotation du moteur synchrone Lip est de 1 tour en 5 minutes. L'alimentation du moteur est faite par l'intermédiaire d'une minuterie (Crouzet) permettant de ralentir la vitesse de polarisation: il est possible d'arrêter la rotation du moteur pendant un temps t_1 variant de 1 seconde à 3 minutes et de maintenir cette rotation pendant un temps t_2 variant également de 1 seconde à 3 minutes. Dans les expériences précédentes $t_2 = 5$ ou 10 secondes, $t_1 = 2$ minutes; on obtient ainsi au moins 3 pointés du galvanomètre pour une même position du curseur du potentiomètre. Le galvanomètre enregistreur inscrit 1 pointé toutes les 38 secondes. Les résultats obtenus par ce mode d'enregistrement ont été fournis dans une précédente publication[9].

β. Emploi du potentiostat

Différents types de potentiostat ont été décrits par LINGANE[2]. Ce sont des régulateurs permettant de maintenir automatiquement constant le potentiel d'une électrode au cours d'une électrolyse. L'appareil utilisé ici a été réalisé par la "Telec"; son principe est le suivant: la différence de potentiel entre l'électrode de platine *A* et l'électrode de référence *C* est maintenue égale à une tension *S* et lui est opposée (Fig. 5); tout déséquilibre entre ces tensions entraîne la déviation du spot d'un galvanomètre G_2 branché dans le circuit: ce spot éclaire deux cellules photoélectriques qui commandent un amplificateur à courant continu constituant la source de tension de l'électrolyse. La déviation du spot agit donc sur l'intensité d'électrolyse de façon à maintenir la différence de potentiel entre les électrodes *A* et *C* égale à la tension imposée *S*.

Bibliographie p. 291

Mode de polarisation b (Fig. 5)

La tension S est remplacée par le potentiomètre entraîné par le moteur synchrone; dans ces conditions la différence de potentiel e entre les électrodes A et C varie linéairement en fonction du temps. L'enregistrement de l'intensité d'électrolyse i fournit directement les courbes $i = \mathrm{f}\,(e)$ (voir Figs. 2 et 4)

Mode de polarisation c (Fig. 6)

Dans ce mode de polarisation, l'intensité d'électrolyse varie linéairement en fonction du temps. Une résistance calibrée est introduite dans le circuit d'électrolyse en série avec la cellule: la chute de tension créée par l'intensité dans cette résistance est maintenue constante par le potentiostat. La tension S est comme précédemment remplacée par le potentiomètre entraîné par le moteur synchrone. Dans ces conditions l'intensité d'électrolyse i varie linéairement en fonction du temps. L'enregistrement de la différence de potentiel e existant entre les électrodes A et C fournit directement les courbes $e = \mathrm{f}\,(i)$. Ce mode de polarisation a été réalisé manuellement par ADAMS et ses collaborateurs[10,11].

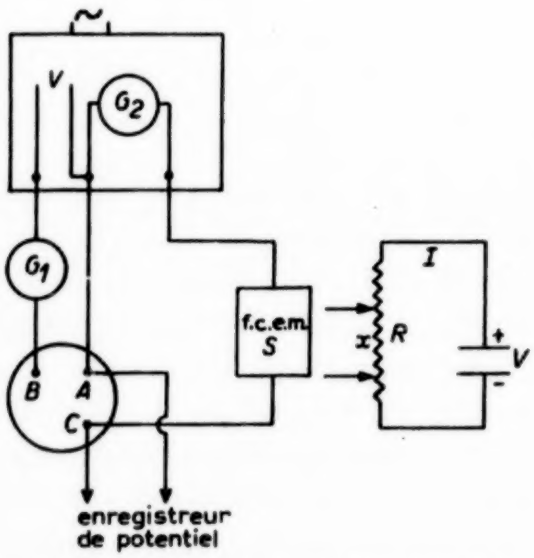

Fig. 5. Schéma de principe. Mode de polarisation b: variation linéaire du potentiel en fonction du temps.

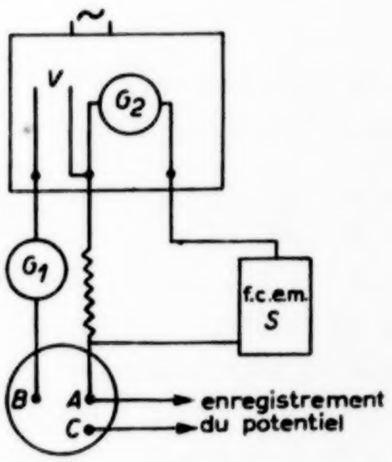

Fig. 6. Schéma de principe. Mode de polarisation c: variation linéaire de l'intensité en fonction du temps.

3. *Dispositif enregistreur*

Un galvanomètre enregistreur à deux voies (Sadir-Carpentier) permet d'enregistrer alternativement deux intensités de courant. L'une est l'intensité d'électrolyse, l'autre est proportionnelle au potentiel de l'électrode de platine A. En effet la différence de potentiel entre cette électrode A et l'électrode de référence C est appliquée à l'entrée d'un amplificateur M E C I (AM) à haute impédance d'entrée (50 MΩ); l'intensité de courant à la sortie de l'amplificateur est proportionnelle à la tension d'entrée. L'amplificateur débite sur une résistance de 100.000 Ω en série avec le galvanomètre.

Les deux sensibilités utilisées sur chacune des voies correspondent à des intensités de 20 et 200 μA d'une part et des tensions de 0,2 et 2 volts d'autre part pour toute l'échelle. Les pointés ont lieu toutes les 19 secondes, soit pour une même voie toutes les 38 secondes.

Bibliographie p. 291

Vérification de la linéarité de l'ensemble potentiomètre—moteur synchrone—minuterie—amplificateur: on constate que les courbes, traduisant les variations de l'intensité en fonction du temps, obtenues en appliquant la tension existant aux bornes du potentiomètre, directement à l'entrée de l'amplificateur sont parfaitement linéaires.

L'appareil que nous venons de décrire peut être utilisé pour le tracé des courbes de polarisation sur platine ou toute électrode solide; dans le cas de l'électrode à goutte de mercure, il conviendra d'étudier l'inertie du potentiostat à l'égard du temps de goutte.

Ces montages déchargent l'expérimentateur, soit d'un pointé manuel fastidieux, soit de corrections, elles aussi longues et fastidieuses. Il permet de plus, dans le cas où l'état de régime n'est pas atteint, d'obtenir cependant des résultats reproductibles.

SUMMARY

A description is given of three methods of recording the polarization curves obtained with platinum electrodes. These methods differ according to the factor which can be varied linearly as a function of time. This factor is either the portion of the potentiometer resistance that is connected to the cell, or the potential of the platinum electrode, or the intensity of the electric current. This factor varies discontinuously as a function of time.

RÉSUMÉ

Trois procédés d'enregistrement des courbes de polarisation sur électrode de platine sont décrits. Ces procédés diffèrent par la grandeur que l'on fait varier linéairement en fonction du temps. Cette grandeur est soit la fraction de résistance du potentiomètre branchée aux bornes de la cellule, soit le potentiel de l'électrode de platine, soit l'intensité de courant de l'électrolyse. Cette grandeur varie d'une façon discontinue en fonction du temps.

ZUSAMMENFASSUNG

Drei Verfahren zur Aufzeichnung der Polarisationskurven an einer Platin-elektrode werden beschrieben. Sie unterscheiden sich durch die Grösse die man lineär mit der Zeit variieren lässt. Diese Grösse ist entweder der Teil des Potentiometerwiderstandes der an die Pole der Zelle geschaltet ist, oder das Potential der Platinelektrode, oder schliesslich die Stromstärke der Elektrolyse. Diese Grösse variiert diskontinuierlich in Funktion der Zeit.

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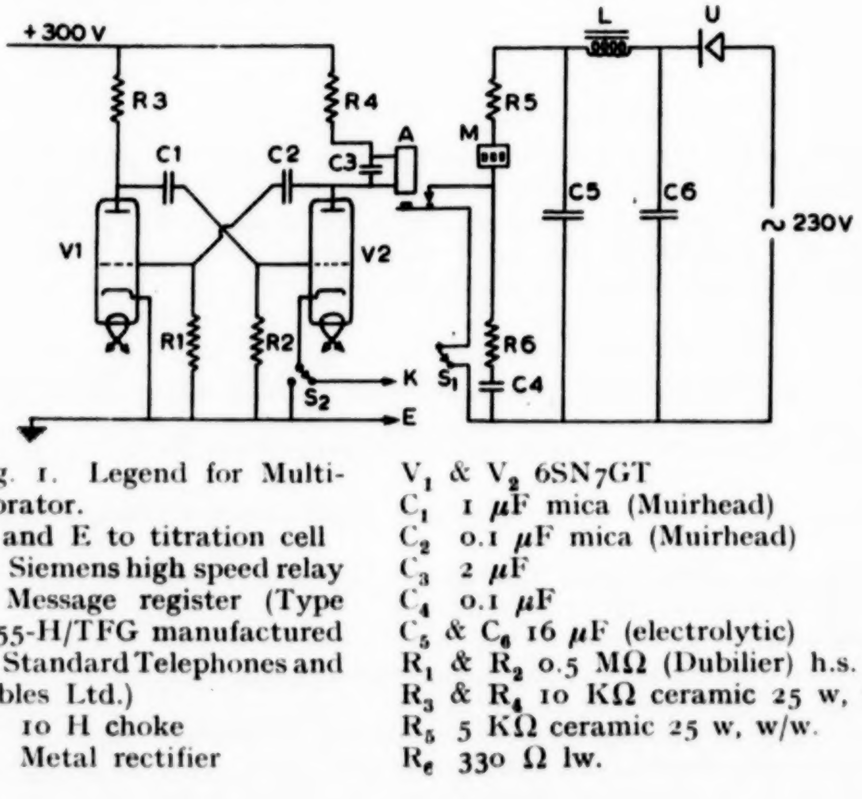
Short Communications

Microdetermination of sodium thiosulphate by the pulse coulometric method

Details of the estimation of 8-hydroxyquinoline in microgram quantities with electrolytically generated bromine using the pulse coulometer, have already been published[1,2]. The same instrument can be used for the estimation of thiosulphate with iodine electrolytically generated from potassium iodide. Excess iodine obtained in the titration after the end-point can be determined, either by the amperometric indicator circuit previously used for detecting excess bromine[2], or with starch as the indicator. While the former method is undoubtedly more sensitive[3], for routine work in which quantities of the order of 500 micrograms sodium thiosulphate in 10 ml of solution have to be determined with an accuracy of 1%, the latter method is more convenient. This method was developed for the determination of sodium thiosulphate or iodine in quantities ranging from 50 to 100 mg per litre to an accuracy of 1%. In this range of concentration the very high sensitivity of the amperometric indicator circuit is both inconvenient and unnecessary.



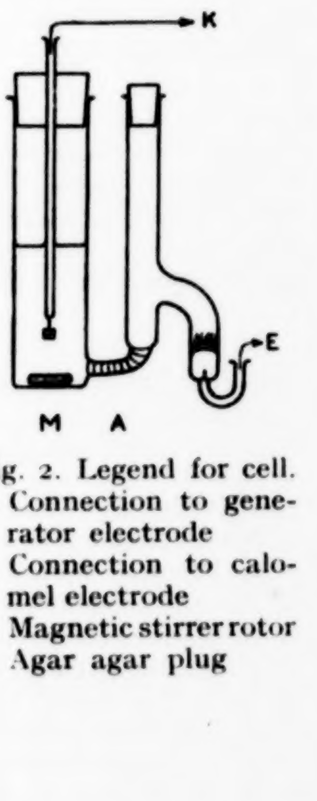


Fig. 1. Legend for Multivibrator.
K and E to titration cell
A Siemens high speed relay
M Message register (Type 4055-H/TFG manufactured by Standard Telephones and Cables Ltd.)
L 10 H choke
U Metal rectifier

V_1 & V_2 6SN7GT
C_1 1 μF mica (Muirhead)
C_2 0.1 μF mica (Muirhead)
C_3 2 μF
C_4 0.1 μF
C_5 & C_6 16 μF (electrolytic)
R_1 & R_2 0.5 MΩ (Dubilier) h.s. lw.
R_3 & R_4 10 KΩ ceramic 25 w, w/w.
R_5 5 KΩ ceramic 25 w, w/w.
R_6 330 Ω lw.

Fig. 2. Legend for cell.
K Connection to generator electrode
E Connection to calomel electrode
M Magnetic stirrer rotor
A Agar agar plug

In order to prevent the number of counts and also the time for titration becoming excessively large, the circuit constants of the pulse coulometer were altered to deliver pulses of about 2000 microcoulombs. A change over switch S_2 (Fig. 1), on the cathode line of the valve V_1 was coupled with switch S_1 on the message register line. The titration cell could be connected or disconnected without interrupting the operation of the multivibrator circuit, thus avoiding variations in the anode resistances arising from intermittent heating. By coupling S_1 to S_2, the message register operated only when the current was diverted through the titration cell.

Procedure. The titration cell is shown in Fig. 2. A platinum foil was used as the generator electrode and a saturated calomel electrode formed the cathode. An agar agar plug isolated the contents of the titration cell from the calomel electrode. The electrolyte used was 10 ml of 10% potassium iodide, 0.25 ml of 1% soluble starch and a measured volume of $N/200$ sodium thiosulphate. The magnetic stirrer M was adjusted to a convenient speed and the electrolysis was started. The passage of each pulse through the cell was shown by a blue colour enveloping the platinum generator electrode, and disappearing almost immediately. Towards the end-point the rate of disappearance of the blue colour was slower, as would be expected. At the end-point the whole solution was suffused with a faint pink colour. This end-point is very reproducible especially when viewed against a white background. It is necessary to carry out a blank on the same volume of solution containing the potassium iodide and starch only. The blank reading was reproducible and was always found to be 3 counts under these conditions. An estimate of the iodine concentration from the pulse size, for the appearance of the pink colour is $7 \cdot 10^{-4}$ grams iodine per litre. This is the limit of the sensitivity for the detection of iodine with starch.

For the bromometric titration of 8-hydroxyquinoline an accuracy of 1% has been claimed[1,2]. In these experiments we have found that an accuracy of 0.5% can be easily obtained. On plotting the number of counts against the number of micrograms of sodium thiosulphate a straight line passing through the origin was obtained. With the pulse size at about 2000 microcoulombs, 750 micrograms of sodium thiosulphate in 10 ml of solution are required to register about 100 counts. In order to obtain an accuracy of 1% the quantities titrated should be greater than 750 micrograms or the pulse size should be suitably reduced.

This method can also be used for the microdetermination of iodine by back-titrating the excess sodium thiosulphate.

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High results in methoxyl determinations on mixtures containing polyhydric alcohols*

During routine determinations of the methoxyl content of fractions of polyhydric alcohols and their methyl ethers obtained after the hydrogenolysis of methyl glycosides[1,2], high values were obtained for fractions where no methyl ethers were expected to be present. Some of these high results were subsequently correlated with the presence of 1,2-propanediol. Methoxyl determinations on samples of pure 1,2-propanediol and several other pure polyhydric alcohols showed that these compounds do, indeed, give methoxyl values ranging from a few to over 30% (see Table I).

TABLE I

Compound analyzed	*% Methoxyl*		
	Calculated	*Found**	*Found***
Anisic acid	20.40	20.43	—
Methyl-tetraacetyl-α-D-glucopyranoside	8.56	8.70, 8.67	—
Methyl-α-D-glucopyranoside	15.98	17.85, 16.78	—
2-Methoxy-ethanol	40.78	69.85, 70.73	—
Sorbitol	0	12.49, 12.87	—
Mannitol	0	11.54, 11.99	—
2,3-Butanediol	0	5.72, 5.78	—
Glycerol	0	10.8 to 26.2	—
1,2-Propanediol	0	26.20, 27.37	22.88
Ethanediol	0	32.6 to 35.1	31.66

* Normal procedure.

** Modified procedure using a second scrubber containing 4 ml of a 0.1 *M* potassium permanganate solution.

Since the original publication by Zeisel[3] many papers have appeared in which improvements in methoxyl determinations are suggested[4]. However, only Araki and Hasi[5] report results in which high values were obtained. Analyzing hexamethyl-***d***-mannitol and hexamethyl-***d***-sorbitol, these authors found that the high values were due to the fact that mannitol and sorbitol themselves give values of 12 to 14%, a result which is confirmed by the present findings (Table I).

The procedure and apparatus used were those described by Hoffman and Wolfrom[6], except that nitrogen was used instead of carbon dioxide as the carrier gas. Results for anisic acid and methyl tetraacetyl-α-D-glucopyranoside (see Table I) show that the method is entirely satisfactory for these compounds.

In experiments with ethanediol, Furter's method for identifying the volatile alkyl iodide formed by reaction with a suspension of the silver salt of 3,5-dinitrobenzoic acid in dry ether[7], was applied. However, silver was liberated and only 3,5-dinitrobenzoic acid could be isolated from the filtered ethereal solution.

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* Issued as N.R.C. No. 4207

Vinyl iodide (b.p. 56°C), having a boiling point close to that of methyl iodide (b.p. 42.5°C) and ethyl iodide (b.p. 72.2°C), was considered as a possible reaction product. This compound possesses a terminal methylene group and can, therefore, be conveniently distinguished from the latter two saturated compounds by the formation of formaldehyde when treated with the periodate-permanganate reagent[8]. When the absorbing solution was replaced by 10 ml of this reagent, a subsequent colorimetric test was positive for formaldehyde, confirming the presence of vinyl iodide. If vinyl iodide is the sole volatile reaction product from polyhydric alcohols it can be removed by interposing a second scrubber containing potassium permanganate solution. However, experiments with ethanediol and 1,2-propanediol (see Table I, modified procedure) show that only a small amount of the interfering substance was removed in this way. After removal of the vinyl iodide, FURTER's method could be applied successfully and ethyl 3,5-dinitrobenzoate (m.p. 92.5-93.5°C, undepressed by an authentic sample of ethyl 3,5-dinitrobenzoate, m.p. 93.5-94.0°C) was isolated in good yield. It is clear, therefore, that the major volatile reaction product is ethyl iodide.

From these results it is apparent that alkoxyl analyses cannot be carried out without the introduction of large errors, if the material to be analyzed contains polyhydric alcohols. Alkyl ethers of polyhydric alcohols, by virtue of forming the free polyol in the reaction with hydrogen iodide, will also give higher than the calculated values. If the polyhydric alcohols contain the 1,2-glycol group, they can be quantitatively removed by oxidation with the periodate-permanganate reagent[8]. The unreacted ethers may then be recovered by extraction from a weakly alkaline solution.

The valuable technical assistance of Mr. M. GRANAT is gratefully acknowledged.

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Determination of oxygen in liquids

The method used by DEINUM AND DAM[1] for determining small quantities of oxygen has been applied until now only to gas samples. By means of a number of changes in the apparatus it proved possible to determine the concentration of oxygen dissolved in liquids, *e.g.* water, hexane, benzene, etc.

The method is based on the removal of dissolved oxygen by means of oxygen-free nitrogen. The mixture of nitrogen and oxygen then passes through the reaction cell, which is filled with copper and an ammoniacal NH_4Cl solution; in this cell a complex, $[Cu_2(NH_3)_4]Cl_2$, is formed. By shaking this colourless complex with air, oxidation occurs and the colour immediately changes to blue, owing to the formation of $[Cu(NH_3)_4]Cl_2$. The concentration of the cupri complex in the combined blue fractions is measured with the aid of a spectrophotometer and compared with a calibration curve, the latter being obtained from measurements on solutions of known concentrations.

The apparatus is made of Pyrex glass. In order to make possible the determination of oxygen dissolved in liquids some changes were made to the model used by DEINUM AND DAM. In Fig. 1, B is the sample container connected with a cooler A. For the connections in the apparatus vacuum tubing covered entirely with "picienwax" is used. All stopcocks and ground-joints are treated with Apiezon-N grease.

The reagents used are those mentioned by UHRIG, ROBERTS AND LEVIN[2], *viz.* an ammoniacal NH_4Cl solution consisting of equal parts of 25% NH_4OH and saturated NH_4Cl solution, which is stored in vessel F. The lift pump is filled with copper fillings; the reaction cell E is packed as densely as possible with pieces of copper of 1 × 1 × 0.1

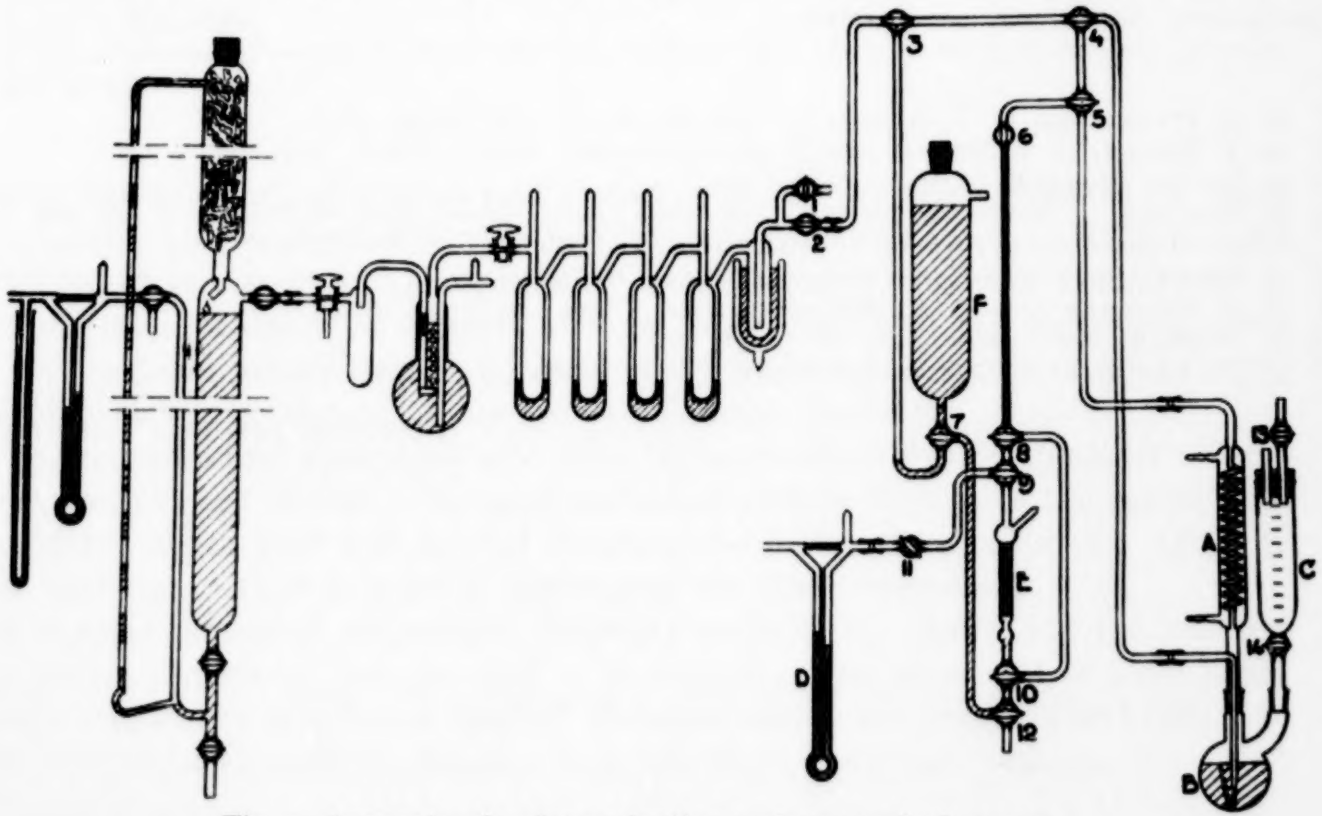

Fig. 1. Apparatus for determination and removal of oxygen.

mm. We used industrial nitrogen freed from oxygen in the lift pump (Fig. 1, left-hand side); ammonia and water are removed subsequently[3].

By means of the lift pump the whole equipment is freed from oxygen; the sample (25-225 ml) is then transferred to a calibrated tube C and from there under pressure to the sample container B. The determination is carried out by passing nitrogen via 2-3-4 through the capillary tube in B and further via 5-6-8-10-E-9-11 to flowmeter D. From this venturimeter the nitrogen flow rate (0.85 l/h) is read. After the oxygen has been removed completely from the sample, the intensity of the blue colour in a standard volume is measured. During the determination the sample container is heated on an electric hot plate in order to facilitate complete removal of the oxygen.

The results of our measurements are shown in Table I, in which the solubility is expressed in ml of oxygen per 1000 ml of solvent; the solvent is in equilibrium with air.

The discrepancies between the results of various authors must be attributed to the differences in the methods of determination applied.

TABLE I

Solvent	*Solubility at room temp.*	
	Values observed	*Values from the literature*
Water	5·99	5·99[4] 6·01[5]
Hexane	60.0	69.0[6]
Ethyl ether	90.0	93·6[7] 94·5[8]
Acetone	45·0	46.6[7] 57·5[8] 48.6[9]
Benzene	47·0	45·8[8]
Methanol	38.0 40.8 42.8	39·3[7] 36.5[9]
Ethyl acetate	53·7	56.8[8]
Nitrobenzene	16.2	15.8[7]
Pyridine	22.0	21.1[7]

We are indebted to Prof. Dr. W. van Tongeren for his comments and to Miss A. Daalder who carried out most of the experiments.

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BUCHBESPRECHUNGEN

Gmelins Handbuch der anorganischen Chemie 8. Auflage 1956. Verlag Chemie, GMBH, Weinheim/Bergstrasse.

Systemnummer 28: Calcium, Teil B - Lieferung 1: Technologie. VIII + 264 Seiten mit 28 Fig. — Kart. DM 147.—.

Systemnummer 32: Zink, Ergänzungsband. XXXVI + 1025 Seiten, 191 Fig. — Kart. DM 570.—. Geb. DM 575.—.

Die Darstellung der *Calcium-Technologie* beginnt mit einem Kapitel über die Aufbereitung der Calciummineralien unter Hervorhebung der Flotation von Flusspat und Calciumphosphat, von denen jener als Rohstoff für die neuerdings in lebhafte Bewegung geratene Fluorchemie, dieses als Dünger oder als Vorstufe der Düngemittelerzeugung Beachtung verdient. Über das Brennen des Kalksteins und das Löschen des Kalks wird sowohl vom Standpunkt der Theorie als auch der Praxis unter Erörterung der verschiedenen Ofensysteme berichtet. Die für die Landwirtschaft wichtigen Stoffe Calciumnitrat, Kalkstickstoff und Calciumphosphat sind besonders im Hinblick auf die modernen Herstellungsverfahren behandelt, doch nicht ausschliesslich vom Standpunkt der Düngererzeugung. Wenn auch die Calcium-Halogen-Verbindungen technisch keine allzu grosse Bedeutung erlangt haben, so hat sich doch eine sehr umfassende Literatur über ihre Herstellung und Verwendung angesammelt, was sich aus der knapp gehaltenen, aber doch ziemlich umfangreichen Zusammenstellung über die Technologie des Fluorids, Chlorids, der Hypochlorite, des Chlorits, Chlorats, Bromids und Jodids ergibt. Von den Schwefelverbindungen werden behandelt: die Sulfide, die Sulfite, das Thiosulfat, das Sulfat. Vom Gips werden alle technisch interessanten Formen nach ihrer Herstellung und Verwendung sowie nach den Vergütungsprozessen, wie z.B. der künstlichen Alterung, der Beeinflussung der Abbindezeit und Härte, der Herstellung von porösem Gips und dergleichen besprochen. Kurze statistische Angaben beleuchten die Bedeutung des Calciumsulfats für die verschiedenen Gewerbe und Industrien. Entsprechend seiner Bedeutung als Grundstoff für eine Reihe von Fabrikationen sind die Grundlagen der Gewinnung von Calciumcarbid und die Durchführung des Carbidprozesses in gedrängter Form geschildert, wobei in vielen Fällen auf ältere Monographien zurückverwiesen wurde. Dadurch war es möglich, auf die Ansätze moderner Arbeitsweisen, wie die Ersetzung der elektrischen Energie durch Sauerstoff, wenigstens hinzudeuten. Bei der Schilderung der Calciumcarbonat-Herstellung liegt das Hauptgewicht auf den Verfahren, welche auf Fällungsvorgängen beruhen, und auf der Reinigung und Verfeinerung des gefällten Produktes. Die zahlreichen Verwendungsarten sind angeführt. Auch organische Calcium-Salze, so die Formiate, das Acetat, Oxalat, Tartrat, die Lactate und Citrate sind kurz beschrieben, ebenso das für die Edelmetallgewinnung und die Schädlingsbekämpfung interessante Calciumcyanid und das Calciumrhodanid.

Fügt man zu dieser gedrängten Inhaltsangabe hinzu, dass ausser den erwähnten Stoffen noch eine Reihe weiterer Verbindungen, wie das Calciumperoxyd, die Borverbindungen, das Silicid, die Arsen- und Antimonverbindungen abgehandelt sind, so ergibt sich eine stattliche Sammlung von technologischem Material über die Herstellung und Verwendung wohl aller Calciumverbindungen, die zur Zeit für die Technik von grösserem Interesse sind.

Es erübrigt sich wohl das grosse Interesse hervorzuheben, das dem *Ergänzungsband* zu dem 1924 erschienenen Hauptband *Zink*, entgegengebracht wird. Unter dem Abschnitt Vorkommen erscheint als neues Kapitel die Geochemie des Elements. Entsprechend der technischen Bedeutung des Zinks ist seine Metallurgie unter Einschluss der vor der eigentlichen Metallgewinnung liegenden Stufen eingehend behandelt worden. Das Werk befasst sich eingehend mit der so wichtigen elektrolytischen Zink-Gewinnung. Die Physik des (hexagonalen) Metalls sowie das elektrochemische Verhalten bilden je ein Kapitel. Besonderes Interesse verdienen auch die Angaben über das korrosive Verhalten im Kapitel chemisches Verhalten. Nach den Abschnitten Zinklegierungen mit Alkali- und Erdalkalimetallen, Oberflächenbehandlung des Zinks und seiner Legierungen, Ionen des Zinks, physiologische Schädigung, Nachweis und Bestimmung, schliesst der Band mit der Beschreibung der Verbindungen des Zinks (255 Seiten). Das ganze Werk ist in übersichtlicher und klarer Weise dargestellt, wodurch seine Verwendung sehr erleichtert wird.

W. Rüedi (Genf)

Neuere maßanalytische Methoden von G. JANDER unter Mitarbeit von E. BLASIUS, E. BRENNECKE, E. EBERIUS, K. FAJANS, N. H. FURMAN, H. G. JERSCHKEWITZ, F. KIENBAUM, H. KLAUS, G. RIENÄCKER, G. SCHWARZENBACH, H. STAMM UND K. STEGEMANN. Vierte umgearbeitete und erweiterte Auflage. Mit 53 Abbildungen und 38 Tabellen. 455 Seiten. Sammlung „*Die chemische Analyse*", Band 33. Stuttgart, F. Enke, 1956, Geh. D.M. 72.—, Ganzl. D.M. 75.—.

Der Band enthält Kapitel über (I) Farb- und Fluoreszenzindikatoren bei der Alkalimetrie; (II) Titration schwacher Basen in Eisessig; (III) Bestimmung kleiner Mengen Wasser; (IV) Cer (IV)-Lösungen als maßanalytisches Oxydationsmittel; (V) Reduktion von Permanganat zu Manganat als Grundlage eines maßanalytischen Verfahrens; (VI) Jodatometrie, Perjodatometrie, Bromatometrie, Bromometrie, Chloramin T, (VII) Metalle als Reduktionsmittel; (VIII) Titrationen mit Chrom(II)- und Titan(III)-salzlösungen; (IX) Oxydations-Reduktions-Indikatoren; (X) Adsorptionsindikatoren; (XI) Ionenaustauscher in der Maßanalyse; (XII) Komplexometrie. An die Kapitel sind, z.Tl. umfangreiche, Literaturverzeichnisse angefügt. Gegenüber der dritten Auflage sind die Kapitel XI und XII neu aufgenommen worden. Außerdem wurden die früher von E. BRENNECKE und R. LANG geschriebenen Kapitel von anderen Autoren verfaßt, bzw. neu bearbeitet.

Ein Band, der unter Mitarbeit so vieler Autoren entstand, ist naturgemäß uneinheitlich. Man findet ganz ausgezeichnete Kapitel neben weniger gut gelungenen. So hält der Rezensent besonders die Kapitel I und II für verbesserungsfähig: Kapitel I bringt eine Darlegung der klassischen Säure-Base-Theorie, Tabellen mit Farb- und Fluoreszenzindikatoren und ferner im Wesentlichen qualitative Angaben über Titrierfehler. Dies gilt auch für den wichtigen Einfluß von Neutralsalzen. In dieser Hinsicht bot der entsprechende Abschnitt in früheren Auflagen wesentlich mehr. Gerade auf die Indikatorfehler und ihre Vermeidung bei Präzisionsbestimmungen sollte man in einer derartigen Monographie eingehen. Im Übrigen vermißt man bei Tab. 3 (S. 9), die die pH-Änderung bei Zugabe bestimmter NaOH-Mengen betrifft, die Angabe des verwendeten Volumens.

In der dritten Auflage wurde das Kapitel II sehr klar vom Standpunkt der Brönsted'schen Säure-Base-Theorie aus behandelt. In der neuen Auflage geschieht das nicht. Es ist aber zwangsläufig schwierig Säure-Base-Reaktionen in Eisessig als Lösungsmittel zu erörtern, wenn man den Begriff der „übersauren Lösungen" ablehnt (S. 23, 24, 34) und die Brönsted'sche Theorie vermeidet. Was über die Unvorstellbarkeit neagitver pH-Werte geschrieben wurde (S. 23), beruht wohl auf einem Mißverständnis. Im Übrigen gibt aber Kapitel II einen guten Überblick über die maßanalytischen Arbeitsweisen im Eisessig als Lösungsmittel.

Im Kapitel III findet man eine eingehende Behandlung der Wasserbestimmung nach Karl Fischer. Außerdem werden die sonstigen Verfahren zur Wasserbestimmung (z.B. Hydrolyse von Säurechloriden, Umsetzung mit Magnesiumnitrid, Natriumamid usw.) erörtert. Die Behandlung ist übersichtlich und klar und der jeweilige Umfang entspricht der analytischen Bedeutung der betreffenden Methode. Ähnlich günstig sind auch die anderen Kapitel zu beurteilen. Auffallend ist, daß die oft sehr brauchbare Oxydation mit alkalischer Permanganatlösung nach STAMM — wie das Literaturverzeichnis erkennen läßt — anscheinend weniger häufig verwendet wird, als sie es verdient. Bemerkenswert sind auch kleinere Abschnitte über reversible Redoxindikatoren für die Bromatometrie und über Reduktorbüretten. Das in theoretischer Hinsicht sehr gründliche Kapitel X (Adsorptionsindikatoren) sollte bezüglich der praktischen Methoden erweitert werden. Das Literaturverzeichnis (mit Stichworten) erleichtert zwar das Auffinden neuerer Arbeiten, eine Ergänzung des Textes wäre aber dennoch erwünscht. Besondere Erwähnung verdienen schließlich die ausgezeichneten Kapitel über Titration mit Cr(II) und Ti(III), sowie über Komplexometrie.

Zum Schluß mag noch gesagt werden, daß die Inhalte zweier Kapitel (Komplexometrie; Ionenaustauscher, vgl. S. 371) von den gleichen Autoren im gleichen Verlag und sogar in der gleichen Buchserie in Monographien behandelt werden. Vielleicht sollte man in späteren Auflagen der „Neueren maßanalytischen Methoden" im Hinblick auf die Preisgestaltung auf eine Wiedergabe dieser Abschnitte verzichten.

H. SCHÄFER (Münster)

Handbuch der analytischen Chemie von W. FRESENIUS UND G. JANDER, Springer Verlag, Berlin 1956. 2. Teil: *Qualitative Nachweisverfahren.*

Bd. IV aβ: Elemente der vierten Hauptgruppe II. Germanium, Zinn. Mit 14 Abbildungen, XV + 210 Seiten. DM 42.—; Ganzleinen DM 46.—.

Bd. VIII ba: Elemente der achten Nebengruppe. Eisen, Kobalt, Nickel. Mit 33 Abbildungen, XIV + 233 Seiten. DM 49.60; Ganzleinen DM 53.60.

3. *Teil*: *Quantitative Bestimmungs- und Trennungsmethoden.*

Bd. III aβ/III b: Elemente der dritten Hauptgruppe II und der dritten Nebengruppe. Gallium, Indium, Thallium, Scandium, Yttrium, Elemente der seltenen Erden (Lanthan - Cassiopeium), Actinium und Mesothor 2, Actinium und Isotope. 2. Auflage. Mit 8 Abbildungen, XV + 452 Seiten. DM 87.—; Ganzleinen DM 91.—.

Wie in den bereits erschienenen Bänden [siehe *Anal. Chim. Acta*, 15 (1956) 499] findet man auch in diesen neu erschienenen Werken eine überaus grosse Auswahl von Methoden. Die modernen Analysenmethoden scheinen sorgfältig ausgewählt zu sein. Der umfangreiche Inhalt ist in der gewohnten Art übersichtlich unterteilt und registriert. Diese Werke sind ein jedem Analytiker, gleichgültig in welcher Richtung er arbeitet, zu empfehlendes Hilfsmittel.

W. RÜEDI (Genf)

BOOK REVIEWS

The determination of toxic substances in air, a manual of I.C.I. practice, by N. STRAFFORD, C. R. N. STROUTS AND W. V. STUBBINGS, Heffer, Cambridge, 1956, 225 pp., 35/—.

Several of the procedures described here have been developed by the Dept. of Scientific and Industrial Research in London, others have been adopted by the Union de chimie pure et appliquée, and the remainder are taken from the literature. All have been tested and applied by I.C.I. over a number of years, a fact that gives this manual its well-deserved authority. The significance of field tests is duly stressed, the provision being made that "any concentration found to be in the region of the accepted safety limit should be taken as indicating an unsatisfactory atmosphere". The introduction gives a summary of sampling procedures and the manner of expressing results. Specific methods for the determination of 49 toxic substances are described. Both editors and publishers are to be congratulated on this book, for which the Chief Inspector of Factories, Sir George Barnett, has written the foreword.

H. A. J. PIETERS (Geleen)

Spectroscopy at Radio and Micro-wave Frequencies by D. J. E. INGRAM, Butterworths Scientific Publications, London, 1955, XII + 332 pp., 45/—.

Despite the emphasis of its title this book is concerned mainly with spectroscopy at micro-wave frequencies, 214 of its pages being devoted to this, while the chapter on radio-frequency spectroscopy is only 40 pages long. A general introductory chapter on spectroscopy is followed by an extensive treatment of micro-wave techniques. Micro-wave production, transmission and detection, micro-wave spectroscopes, the principles and theory of micro-wave gas spectroscopy, paramagnetic and ferromagnetic resonance. These chapters are intended for the non-specialists but the treatment is such that this often can only mean the non-specialist physicist.

Of most interest to readers of *Analytica Chimica Acta* will undoubtedly be the final chapter which contains an illuminating discussion and comparison of the application of the techniques, including an assessment of their value for chemical analysis. The book is well produced, clearly printed and the chapters on electron resonance are very up-to-date.

D. J. FERRETT (Harwell)

DIRECT TITRATION OF MERCURY(I) WITH POTASSIUM PERMANGANATE

by

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The oxidation of mercurous mercury with potassium permanganate was applied by KELLEY *et al.*[1] to the titration of permanganate in presence of vanadate and chromate in steel analysis because mercurous nitrate was found to reduce only permanganate and not the other two compounds. In this titration the end-point is determined potentiometrically. Owing to the fact that the reduction products of permanganate are not known with certainty, the mercurous solution should be standardized, against a standard permanganate solution. From the data obtained from known concentrations of potassium permanganate and mercurous nitrate and from the oxidizing power of the solution towards ferrous sulphate after titration with potassium permanganate, KELLEY could deduct the following equation:

$$4\ \mathrm{Mn^{VII}} + 14\ \mathrm{Hg^{I}} = 3\ \mathrm{Mn^{IV}} + 1\ \mathrm{Mn^{II}} + 14\ \mathrm{Hg^{II}}$$

The direct titration of mercury(I) with potassium permanganate has not yet been applied as a method for the determination of the former and it is the aim of the present investigation to study this reaction.

EXPERIMENTAL

Preparation and standardization of solutions

1. Standard potassium permanganate solutions were prepared by a method similar to that of STAMM[2] and standardized by sodium oxalate of AnalaR grade following the procedure recommended by FOWLER AND BRIGHT[3]. The solutions used were 0.0991*N* and 0.0766*N*. The normality is based on the assumption that the change in valency is five ($\mathrm{Mn^{VII}} \rightarrow \mathrm{Mn^{II}}$).
2. Mercurous nitrate solutions were prepared from mercurous nitrate by dissolving 30 g of the solid in one litre of twice distilled water containing 10 ml of AnalaR concentrated nitric acid. The solution was then filtered through a 1 G3 sintered glass funnel.
   The concentration of mercurous mercury was determined by precipitation as chloride following the method given by KELLEY[1]. The mercurous solutions titrated possessed the following normalities 0.1071, 0.0514, 0.0428, 0.0268, and 0.0214*N*.
3. 9*N* sulphuric acid prepared by diluting the AnalaR product.
4. 2% sodium fluoride was prepared by dissolving 20 g of the commercial solid in one litre of redistilled water.

Procedure of titration

A volume of the mercurous solution is placed in a conical flask and mixed with a solution consisting of 50-75 ml of 2% NaF + 5-10 ml 9*N* H_2SO_4 so that the whole volume is 100 ml. The clear solution is then titrated with potassium permanganate. Owing to the sluggishness of the reaction near the end-point, especially with the more concentrated solutions, the permanganate should be added cautiously as the end-point is approached. The end-point is detected by the appearance of a pink colour which lasts for ∿ 40 seconds.

It is advisable not to add the sodium fluoride solution before the sulphuric acid as otherwise mercurous fluoride is formed which hydrolyses to mercurous oxide and dissolves slowly in the acid, leaving the solution turbid. It is also advisable to carry out blank experiments with all the reagents used except the mercurous nitrate.

RESULTS

On titrating mercurous solutions in presence of sulphuric acid with potassium permanganate, the reaction medium remains at first colourless due to the fact that the permanganate is reduced to the manganous state. However, long before the end-point is reached, the solution turns yellow and then brownish rendering it impossible to detect the end of the titration, contrarily to the case when the solution remains colourless.

Further, the brown colour due to partial production of manganese dioxide renders this process inaccurate. Mercurous mercury is not a strong enough reducing agent to bring about complete reduction of Mn^{VII} to Mn^{II}.

The redox potential of the mercuric-mercurous couple amounts to 0.92 V[4], a value which lies between that of the Fe^{+3}-Fe^{+2} system (0.771 V[4], Fe^{+2} reducing Mn^{+7} to Mn^{+2}) and the MnO_2-Mn^{+2} couple (1.23 V[4], Mn^{+2} reducing Mn^{+7} to Mn^{+4})[5]. It is concluded that reduction of permanganate by mercurous mercury gives rise to reduction products intermediate between Mn^{+2} and Mn^{+4} and that the reaction can be checked at the manganic state if the latter is complexed by the aid of fluoride ions. If this is the case, then one may obtain better results by performing the titrations in presence of fluoride. Fluoride was applied by MÜLLER[5] in the titration of manganous salts with potassium permanganate. Because the manganic fluoride complex is almost colourless in very dilute acidic solutions, it becomes possible to trace the end-point visually. Under these conditions, permanganate is reduced to trivalent manganese and the reaction may be written as:

$$Mn^{VII} + 4\,Hg^{I} = Mn^{III} + 4\,Hg^{II}$$

This method, the results of which are shown in Tables I-III, appears to be reliable within 0.5% from results obtained by the chloride method.

Effect of mercurous ion concentration

Table I represents the titration of different volumes of the mercurous solutions at fixed acid and fluoride concentrations. From these data it is apparent that good results are only obtained with smaller volumes or dilute solutions. This occurs because, with high mercurous concentrations, during the titration the solution becomes pink near the end-point rendering it very difficult to observe the end-point visually. Furthermore, the reaction becomes sluggish. When the final normality of the mercurous mercury after mixing with other solutions is 0.005*N* or lower, the reaction is rapid and the end-point sharp.

References p. 304

TABLE I

EFFECT OF MERCUROUS CONCENTRATION AT THE END-POINT
NaF: 75 ml of 2% soln., H_2SO_4: 5 ml of $9N$ acid

Mercurous nitrate		*0.0991N*[a] *KMnO₄ consumed ml*	*Theoretical end-point ml*	*Error %*
ml	*Normality*			
10	0.0514	6.47	6.48	−0.15
20	0.0514	12.93	12.96	−0.23
25	0.0514	—	16.20	—
10	0.0428	5.38	5.40	−0.37
20	0.0428	10.75	10.80	−0.46
25	0.0428	13.46	13.50	−0.30
10	0.0268	3.36	3.38	−0.59
20	0.0268	6.73	6.76	−0.44
25	0.0268	8.42	8.45	−0.36
10	0.0214	2.72	2.70	0.74
20	0.0214	5.42	5.40	0.37
25	0.0214	6.75	6.75	nil

[a] This normality should be multiplied by 0.8 in calculating the theoretical end-point. This normality is based on the change $Mn^{+7} \rightarrow Mn^{+2}$, while theoretically we get $Mn^{+7} \rightarrow Mn^{+3}$.

Effect of concentration of sodium fluoride

Table II shows the effect of sodium fluoride on the end-point when both the acid and the mercurous ion concentrations are kept constant. When the concentration of the sodium fluoride solution is 0.2%, the end-point is reached 0.86% before the theoretical value. Concentrations of NaF as high at 1.8% in the presence of $0.3N$ H_2SO_4 give rise to a turbid solution, rendering it difficult to detect the end-point. When the acid concentration is raised to $0.5N$ H_2SO_4, the end-point is attained 1.15% later than the theoretical.

The optimum concentration of sodium fluoride in presence of 0.5-$1N$ H_2SO_4 is 1-1.5%.

TABLE II

TITRATION OF 10 ml $0.0428N$ Hg^I WITH $0.0766N$ $KMnO_4$ IN PRESENCE OF VARYING CONCENTRATIONS OF NaF

2% sodium fluoride ml	*9N H₂SO₄ ml*	*KMnO₄ consumed ml*	*Theoretical end-point ml*	*Error %*
10	5	6.92	6.98	−0.86
25	5	6.94	6.98	−0.57
50	5	6.95	6.98	−0.43
75	5	6.95	6.98	−0.43
100	5	7.06	6.98	+1.15

Effect of sulphuric acid concentration

Table III contains the results obtained on changing the concentration of sulphuric acid from 0.1 to $2N$. With $0.1N$ sulphuric acid, the solution before titration was turbid yellow, due to the precipitation of mercurous fluoride and it was not possible to observe the end-point. With a $1.9N$ sulphuric acid concentration, the end-point becomes delayed 2.58%. When on the other hand the sulphuric acid concentration is made 0.5-$1N$, the end-points coincide fairly well with the theoretical values.

TABLE III

TITRATION OF 10 ml 0.0428N Hg^I WITH 0.0766N $KMnO_4$ IN PRESENCE OF VARYING CONCENTRATIONS OF H_2SO_4

2% NaF *ml*	*9 N H_2SO_4* *ml*	*$KMnO_4$ consumed* *ml*	*Theoretical end-point* *ml*	*Error* *%*
75	1.1	—	6.98	—
75	5	6.95	6.98	−0.43
75	11	6.99	6.98	+0.14
75	22	7.16	6.98	+2.58

Effect of temperature

It is recommended to carry out the experiment between 35°C and 50°C since at lower temperatures the reaction becomes sluggish. Further, at lower temperatures, sodium fluoride possesses a small solubility so that the optimum amount cannot be applied, and when it is added, the solution becomes turbid. At higher temperatures than 50°C, on the other hand, larger volumes of permanganate are consumed before the end-point is reached.

SUMMARY

Mercurous solutions can be successfully titrated with potassium permanganate in presence of 0.5-1N H_2SO_4 and 1-1.5% NaF at 35-50°C. Sharp end-points are obtained when the maximum concentration of monovalent mercury after mixing with the other reagents is 0.005N. At higher concentrations the reaction is sluggish and the end-points are not sharp.

RÉSUMÉ

Le mercure(I) peut être titré par le permanganate de potassium, en présence de H_2SO_4 0.5-1N et de NaF (1 à 1.5%) à 35-50°C. On obtient des points finals nets avec une concentration en mercure(I) inférieure à 0.005N (après addition des autres réactifs). Pour des concentrations plus fortes, la réaction est lente et le point final peu précis.

ZUSAMMENFASSUNG

Quecksilber(I)-Lösungen können erfolgreich mit Kaliumpermanganat in Anwesenheit von 0.5-1N H_2SO_4 und 1-1.5% NaF bei 35-50°C titriert werden. Scharfe Endpunkte werden erreicht, wenn die maximale Konzentration des einwertigen Quecksilbers nach Zugabe der Reagenzien 0.005N beträgt. Bei höheren Konzentrationen ist die Reaktion träge und die Endpunkte sind unscharf.

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MICRO-VOLUMETRIC DETERMINATION OF MERCURY WITH THIONALIDE

by

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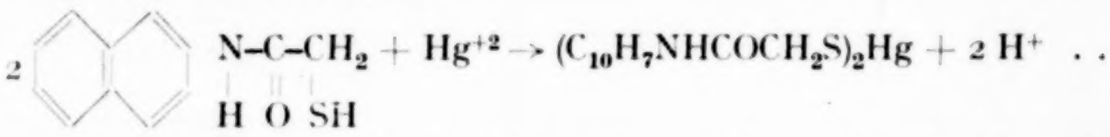
INTRODUCTION

This research was undertaken in continuation of our studies concerning the application of thionalide (thioglycolic acid β-aminonaphthalide) as a reagent in inorganic micro-analysis. After having evolved micro-volumetric and micro-gravimetric methods for the determination of lead[1,2] and a micro-gravimetric method for the determination of thallium[3] with this reagent, we attempted the elaboration of a micro-method for mercury.

As shown by R. BERG AND W. ROEBLING[4] Hg^{+2} reacts in an acid medium with thionalide, forming a white precipitate:



$$2\,C_{10}H_7\underset{H}{N}-\underset{O}{\overset{\|}{C}}-\underset{SH}{CH_2} + Hg^{+2} \rightarrow (C_{10}H_7NHCOCH_2S)_2Hg + 2\,H^+ \quad . . \ (1)$$

The washed precipitate may be dissolved in a mixture of acetic acid and a mineral acid and the liberated thionalide oxidized with standard iodine solution to dithionalide:

$$2\ C_{10}H_7NHCOCH_2SH + I_2 \rightarrow$$
$$\rightarrow C_{10}H_7NHCOCH_2S - SCH_2CONHC_{10}H_7 + 2\ HI \quad . . . . \ (2)$$

Mercury is calculated from the volume of iodine solution participating in reaction (2).

After a systematic study of all the factors affecting this determination, such as: 1) the acidity of the solution containing the Hg^{+2} ions, 2) the temperature of precipitation, 3) the amount of the reagent and the method of its introduction, 4) the temperature of filtration, 5) the wash liquid used, 6) adequate dilution of the solution containing the liberated thionalide in order to obtain a clear end-point, we have elaborated an exact micro-volumetric method for the determination of mercury.

EXPERIMENTAL

Reagents and standard solutions

1. Mercuric chloride solution (prepared by dissolving 2.707 g of $HgCl_2$ in bi-distilled water and making up to 1 litre. The solution contains 2 mg Hg^{+2} per ml).
2. Nitric acid $2N$.
3. Thionalide.
4. Glacial acetic acid.
5. Glacial acetic acid-hydrochloric acid $5N$ (mixture 5:1).
6. Sulphuric acid (1:5).
7. Iodine solution $0.1N$.
8. Pure carbon dioxide gas (if generated in a Kipp Apparatus, the gas should be washed by bubbling through a saturated solution of sodium bicarbonate).
9. Potassium iodide.

References p. 311

10. Standard 0.01N potassium iodate-iodide solution (prepared by dissolving 0.3567 g KIO_3 in 200 ml H_2O containing 1 g NaOH and 2-3 g KI, and making up to 1 litre).
11. 1% starch solution.
12. Standard 0.01N sodium thiosulphate solution (prepared by diluting a 0.1N solution and checked against Reagent No. 10).
13. Bi-distilled water was used throughout.

Procedure recommended for the micro-volumetric determination of mercury

To the aqueous solution of mercury (-ic) chloride (1-3 mg mercury in 0.5-1.5 ml solution) in a small Pyrex glass beaker* 1.5 ml of nitric acid 2N are added and the volume made up with bi-distilled water to 8 ml approximately. The sample is heated on an asbestos mat to just below the boiling temperature (caution: vigorous boiling causes squirting). The precipitation of mercury is next effected by the addition of a freshly prepared solution of thionalide in glacial acetic acid, using an excess of 200%-300% of the reagent (*i.e.* 6.50-8.66 mg thionalide per mg Hg^{+2})**. The reagent solution is introduced dropwise from a pipette, the sample being stirred continuously with a glass rod. Particular care must be taken that no drop of the reagent fall on the sides of the beaker or on the stirring rod. Stirring and heating are continued until the solution clears. The solution is filtered through a glass filterstick (medium porosity)***, which has been pre-heated by sucking boiling bi-distilled water through it and dipped into the solution until the filterplate nearly touches the bottom of the beaker; the precipitate tends to collect at the top of the solution (Fig. 1). On applying suction, the solution is filtered off before the precipitate settles on the filterplate, thus preventing the excess of thionalide from settling out on the plate and slowing down the filtration. The precipitate, the filterstick, the glass rod and the beaker are washed immediately 10-15 times with boiling bi-distilled water, using portions of 4 ml each. The last portion of wash liquid is collected in a small test tube and examined for the presence of thionalide, as follows: 0.5 ml of the wash liquid is introduced into a depression of a black, glazed porcelain spot plate, 1 drop of sulphuric acid (1:5) and 1 drop of 0.1N iodine solution are added and the mixture stirred vigorously with a glass rod. In the presence of at least 10 micrograms (γ) of thiona-

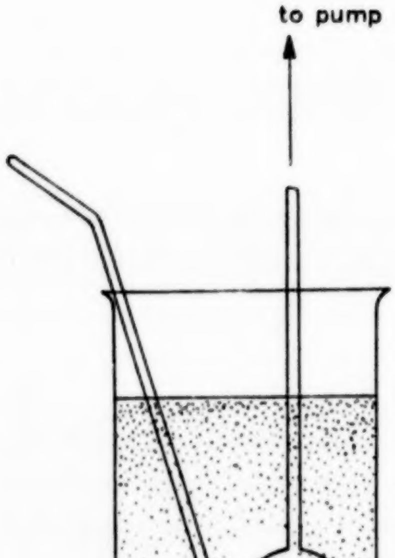


Fig. 1. Apparatus for filtration.

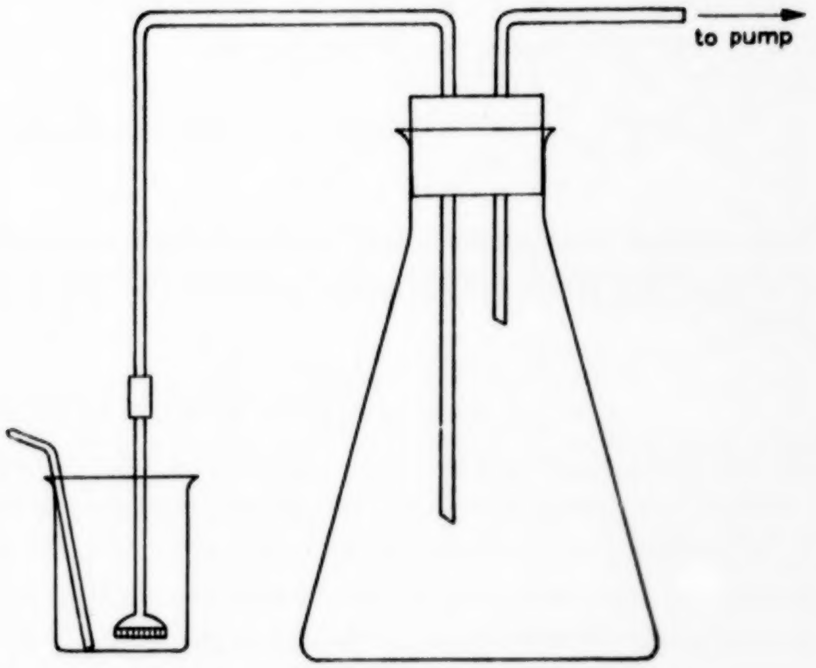


Fig. 2. Apparatus for filtration.

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* Dimensions of the beaker: height 32 mm, diameter 25 mm.

** Preparation of the thionalide solution: the appropriate amount of thionalide is dissolved in 1 ml of glacial acetic acid in a small Pyrex glass beaker (gentle heating is applied).

*** The dimensions of the filterstick used were: overall diameter 10 mm; outside stem diameter 4 mm; overall height 110 mm. All filtersticks used were U.S.A. produce, made by Corning glass works.

References p. 311

lide, a white, floccular precipitate of dithionalide is formed within two minutes; the precipitate is best observed in daylight:

$$2\ C_{10}H_7NHCOCH_2SH + I_2 \rightarrow C_{10}H_7NHCOCH_2S\text{-}SCH_2CONHC_{10}H_7 + 2\ HI$$

If no thionalide is detected, the filterstick is detached from the suction system and the beaker, stirring rod and filterstick are washed down with 4-5 ml of the hot acid mixture (Reagent No. 5). Gentle heating and stirring accelerate the solution of the precipitate. The filterstick is now connected again to the suction system and the solution of the thionalide sucked through it into a dry 125 ml Erlenmeyer flask (Fig. 2). Beaker, stick and glass rod are then washed repeatedly with the acid mixture (Reagent No. 5), 3 × 3 ml, each time sucking the wash liquid through the stick into the Erlenmeyer flask.

The flask is now detached from the suction system, a capillary tube leading to a source of carbon dioxide gas is introduced into the solution and carbon dioxide (Reagent No. 8) bubbled through it.

Approximately 20 mg of potassium iodide are now added and 0.01 *N* standard potassium iodate-iodide solution introduced from a micro-burette, graduated to 0.01 ml*, until excess of iodine is apparent from the yellow colour of the liquid. The mixture is next diluted to 40 ml approx. with bi-distilled water, 1 ml 1% starch solution added and the solution back-titrated with 0.01 *N* sodium thiosulphate solution to the disappearance of the blue colour, using a similar micro-burette. For the quantities and reagents used, it was found necessary to deduct a blank** equal to 0.015 ml of 0.01 *N* potassium iodate-iodide solution. 1 ml of 0.01 *N* potassium iodate-iodide solution → 1.003 mg mercury. The time required for one determination is 45 minutes to 1 hour approximately.

Remark

After use the filterstick is rinsed by sucking bi-distilled water through it. Table I shows some characteristic results obtained by the above method.

TABLE I

MICRO-VOLUMETRIC DETERMINATION OF MERCURY WITH THIONALIDE

Exp. No.	*Excess of thionalide %*	*Hg present mg*	*Hg found mg*	*Hg difference mg*	*Relative error %*
1	200	1.000	1.003	+0.003	+0.3
2	200	1.000	0.993	—0.007	—0.7
3	300	1.000	1.003	+0.003	+0.3
4	300	1.000	0.995	—0.005	—0.5
5	200	2.000	1.994	—0.006	—0.3
6	200	2.000	2.010	+0.010	+0.5
7	300	2.000	2.004	+0.004	+0.2
8	300	2.000	1.990	—0.010	—0.5
9	200	3.000	2.997	—0.003	—0.1
10	200	3.000	3.015	+0.015	+0.5
11	300	3.000	2.997	—0.003	—0.1
12	300	3.000	3.012	+0.012	+0.4

Conclusion

As indicated by Table I, results are exact (maximum relative error ± 0.5% for 2-3 mg Hg^{+2} and ± 0.7% for 1 mg Hg^{+2}).

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* The micro-burettes employed were Blue Line "Exax" burettes (U.S.A.), 5 ml capacity, with a graduation interval of 0.01 ml and a platinum alloy delivery tip, giving approx. 100 drops per ml.

** The blank must be determined experimentally, according to the quality of the reagents employed.

The method was established with samples containing 1-3 mg of mercury; it was next tested on samples containing 4 mg of mercury. The results obtained were high, due to both the increased concentration of thionalide in the solution and the larger volume of mercury thionalide precipitate formed. Nevertheless, correct results are obtained by doubling the volume of the sample solution, prior to the precipitation; to this end a larger Pyrex glass beaker must be used (approx. double capacity of the beaker described above).

Table II shows some characteristic results obtained.

TABLE II

MICRO-VOLUMETRIC DETERMINATION OF MERCURY IN SAMPLES CONTAINING 4 mg Hg^{+2}

Exp. No.	*Excess of thionalide* %	*Hg present* *mg*	*Hg found* *mg*	*Hg difference* *mg*	*Relative error* %
1	200	4.000	4.016	+0.016	+0.4
2	200	4.000	3.996	—0.004	—0.1
3	300	4.000	3.992	—0.008	—0.2
4	300	4.000	4.020	+0.020	+0.5

Conclusion

As indicated by Table II, results are exact (maximum relative error ± 0.5%).

With a view to establishing the influence of larger excess of thionalide on the accuracy of results, experiments were carried out with excess of the reagent up to 500%. In order to avoid high results, certain adjustments in the volume of wash liquid, as set out in Table III, must be made.

Table III shows some characteristic results obtained.

TABLE III

MICRO-VOLUMETRIC DETERMINATION OF MERCURY WITH 400%-500% EXCESS OF THIONALIDE

Exp. No.	*Excess of thionalide* %	*Hg present* *mg*	*Hg found* *mg*	*Hg difference* *mg*	*Relative error* %	*Approx. volume of the sample solution* *ml*	*Approx. volume of wash liquid* *ml*
1	400	1.000	0.997	—0.003	—0.3	8	40-60
2	500	1.000	1.000	—	—	8	40-60
3	400	2.000	2.006	+0.006	+0.3	8	40-60
4	500	2.000	2.010	+0.010	+0.5	8	40-60
5	400	3.000	3.012	+0.012	+0.4	8	80-120
6	500	3.000	3.015	+0.015	+0.5	8	80-120
7	400	4.000	4.080	+0.080	+2.0	16	80-120
8	500	4.000	4.120	+0.120	+3.0	16	80-120

Conclusion

For 1-3 mg of mercury, provided that, for samples of 3 mg mercury, the adequate modification in washing the precipitate is made, results are exact (maximum relative error ± 0.5%). For 4 mg of mercury results are high.

Discussion of the factors affecting the determination of mercury by the proposed method

1. 1-3 mg of mercury and an excess of thionalide 200%-300% were chosen as optimum limits for the method proposed, due to the following considerations:

a) samples over 3 mg of mercury gave a precipitate of mercury thionalide, which was too bulky to be handled comfortably under the experimental conditions established. As shown by Table II, samples of 4 mg of mercury may still be determined successfully, provided the volume of the sample solution is doubled (a larger Pyrex glass beaker is used),

b) Whenever an excess of thionalide exceeding 300% is employed for samples of 3 mg mercury, washing must be doubled, thus making the determination tedious. For samples of 4 mg Hg^{+2}, even increased washing does not give correct results.

2. The washing recommended in the above mentioned procedure was on the whole found adequate in the experiments carried out. In order, however, to prevent any unsuccessful determination, due to incomplete washing, the last portion of the wash liquid was tested for the presence of thionalide (see recommended procedure).

3. Atmospheric oxidation, from the moment potassium iodide is added, is completely eliminated by bubbling carbon dioxide through the solution to be titrated, beginning before the introduction of the potassium iodide and continuing throughout the titration. This also provides efficient stirring of the solution during titration.

4. The titrated solution is diluted to 40 ml approximately with bi-distilled water, before back-titration with sodium thiosulphate. This dilution was found adequate for obtaining a clear end-point.

MICRO-VOLUMETRIC DETERMINATION OF MERCURY IN THE PRESENCE OF ZINC AND CADMIUM

Prompted by the practical importance of the Hg-Zn and Hg-Cd amalgams, we have examined, in continuation of our research, the possibility of the determination

TABLE IV

MICRO-VOLUMETRIC DETERMINATION OF MERCURY IN THE PRESENCE OF ZINC

Exp. No.	*Excess of thionalide, %*	*Hg present, mg*	*Zn* present approx., mg*	*Hg found, mg*	*Hg difference, mg*	*Relative error, %*
1	200	3.000	3	2.985	—0.015	—0.5
2	200	3.000	3	3.003	+0.003	+0.1
3	200	3.000	9	2.985	—0.015	—0.5
4	200	3.000	9	3.003	+0.003	+0.1
5	200	3.000	15	2.994	—0.006	—0.2
6	200	3.000	15	3.015	+0.015	+0.5
7	200	3.000	24	2.994	—0.006	—0.2
8	200	3.000	24	3.003	+0.003	+0.1
9	200	3.000	30	3.003	+0.003	+0.1
10	200	3.000	30	2.991	—0.009	—0.3
11	200	3.000	45	3.009	+0.009	+0.3
12	200	3.000	45	2.994	—0.006	—0.2
13	200	3.000	60	2.988	—0.012	—0.4
14	200	3.000	60	2.997	—0.003	—0.1
15	200	3.000	90	3.003	+0.003	+0.1
16	200	3.000	90	3.006	+0.006	+0.2
17	200	3.000	105	3.015	+0.015	+0.5
18	200	3.000	105	3.012	+0.012	+0.4
19	200	3.000	120	3.024	+0.024	+0.8
20	200	3.000	120	3.027	+0.027	+0.9

*Zn^{+2} was introduced into the sample in the form of sulphate.

of mercury, by the method elaborated, in the presence of zinc and cadmium respectively (A and B).

A. Micro-volumetric determination of mercury in the presence of zinc

The above mentioned method, elaborated for the determination of mercury, may be successfully applied in the presence of zinc, provided the amount of zinc (Zn^{+2}) in the sample does not exceed 100 mg (see Table IV, Exp. 1-18).

Table IV shows some characteristic results obtained.

Conclusion

As indicated by Table IV, results are exact (maximum relative error ± 0.5%).

B. Micro-volumetric determination of mercury in the presence of cadmium

The above mentioned method, elaborated for the determination of mercury, may be successfully applied in the presence of cadmium, provided the amount of cadmium (Cd^{+2}) in the sample does not exceed 15 mg, and the following modification is made: 2 ml of 2*N* HNO_3 are introduced into the sample containing the Hg^{+2} and Cd^{+2} ions, instead of 1.5 ml, as indicated in the procedure recommended* (see Table V, Exp. 1-8).

Table V shows some characteristic results obtained.

TABLE V

MICRO-VOLUMETRIC DETERMINATION OF MERCURY IN THE PRESENCE OF CADMIUM

Exp. No.	*Excess of thionalide* %	*Hg present* mg	*Cd** present approx.* mg	*Hg found* mg	*Hg difference* mg	*Relative error* %
1	200	3.000	3	3.012	+0.012	+0.4
2	200	3.000	3	2.991	−0.009	−0.3
3	200	3.000	6	3.006	+0.006	+0.2
4	200	3.000	6	2.988	−0.012	−0.4
5	200	3.000	9	3.015	+0.015	+0.5
6	200	3.000	9	2.991	−0.009	−0.3
7	200	3.000	15	3.003	+0.003	+0.1
8	200	3.000	15	3.012	+0.012	+0.4
9	200	3.000	18	3.018	+0.018	+0.6
10	200	3.000	18	3.024	+0.024	+0.8

Conclusion

As indicated by Table V, results are exact (maximum relative error ± 0.5%).

Remark

Attempts to elaborate a micro-gravimetric method for the determination of mercury with thionalide were unsuccessful due to, probably, occlusion or adsorption effects of contaminating substances, which could not be removed by washing.

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* Determination of mercury, in the absence of cadmium, in a sample containing 2 ml of 2*N* HNO_3 instead of 1.5 ml proved, that the modification made has no influence on the accuracy of the results.

** Cd^{+2} was introduced into the sample in the form of sulphate.

References p. 311

ACKNOWLEDGEMENT

We wish to express our appreciation to Mrs. MAGDA ARIEL for her valuable help and advice in this work.

SUMMARY

The authors have elaborated an exact micro-volumetric method for the determination of mercury with thionalide.

RÉSUMÉ

Les auteurs ont élaboré une micro-méthode volumétrique exacte pour la détermination du mercure au moyen de thionalide.

ZUSAMMENFASSUNG

Die Verfasser haben eine exakte mikro-volumetrische Methode zur Bestimmung des Quecksilbers mit Thionalid ausgearbeitet.

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INVESTIGATION OF CHEMICAL SEPARATION METHODS FOR Ca AND Sr.

QUANTITATIVE DETERMINATION OF BOTH ELEMENTS IN Ca-Sr MIXTURES BY THE ISOTOPIC DILUTION METHOD

by

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INTRODUCTION

Separation methods for Ca and Sr in mixtures of both elements are numerous. Most are based on the extraction of the dry nitrates with suitable solvents, while some use separation by selective precipitation as nitrates, sulfates, ferrocyanides or chromates.

Ethyl alcohol, isobutyl alcohol, *n*-butyl alcohol-1-glycol ether and acetone have been investigated as solvents for the extraction of $Ca(NO_3)_2$ from the dry nitrate mixture. RAWSON[1] described the separation of the nitrates using nitric acid of density 1.46. FRESENIUS[2] and NOLL[3] used a 1 : 1 ethyl alcohol-ether mixture, while BROWNING[4] studied the separation by adding isoamyl alcohol to the saturated solution of the nitrates and subsequent boiling. Methods for the separation of carbonates using nitric acid, of sulfates using bitartrate, of chlorides with *n*-butyl alcohol saturated with hydrochloric acid, and of chromates with acetone-water and ethyl alcohol-water mixtures are also reported.

Precipitation methods are described using $(NH_4)_2SO_4$, K_2SO_4, a mixture of $(NH_4)_2SO_4$ and $(NH_4)_2C_2O_4$ or $K_4[Fe(CN)_6]$.

Precipitation from homogeneous solution with dimethyl sulfate has been investigated by ELVING AND VAN ATTA[5]. The precipitation of $Sr(NO_3)_2$ from a saturated solution by addition of fuming nitric acid has been studied by WILLARD AND GOODSPEED[6]. Selective precipitation of $SrCrO_4$ was first reported by FRESENIUS AND RUPPERT[7], and studied by KOLTHOFF[8] and DAVIS[9].

From a survey of the literature, it is obvious that there is little agreement on the value of the reported methods for the quantitative separation of calcium and strontium. In this study the quantitative separation of both elements by some of the most promising chemical procedures has been investigated, using radiochemical tracer techniques. Separation by chromatography and ion exchange was not investigated.

EXPERIMENTAL

Choice of the tracers and activity measurements

For the study of quantitative separation by different procedures, ^{45}Ca and ^{89}Sr were used as tracers. Both isotopes were obtained from A.E.R.E.-Harwell and were not carrier-free. Consequently adequate corrections were made for the introduced amounts of carriers. These were found to be 1.24 mg Sr, respectively 0.92 mg Ca per 100 μl of tracer solution. In the preparation of the latter, care has been taken that the active isotopes were present in the same chemical form as the inactive isotopes to be separated.

The activity of the samples was measured with a Tracerlab G.M.2 tube and SC-7-"100" Scaler. The samples were mounted in a reproducible way so as to minimize errors due to backscattering, air-absorption and geometry. Correction for self-absorption was made according to the method of ATEN Jr[10].

Standard solutions

$CaCO_3$ and $Sr(NO_3)_2$ Merck analytical grade were used for the preparation of standard solutions. The purity of the reagents was checked by spectrographic analysis. The Ca content of the $Sr(NO_3)_2$ appeared to be less than 0.001%, the Sr content of the $CaCO_3$ was slightly higher. Standard solutions were prepared containing, per ml, 10 mg Ca and 10 mg Sr as their nitrates. From these standard solutions two series of three solutions were prepared. The Ca to Sr proportion was respectively 20 : 80, 50 : 50 and 80 : 20, the total amount of ions being kept constant at 100 mg. One series contained tracer ^{45}Ca, the other contained ^{89}Sr, so as to be able to control the purity of the separated fractions.

RESULTS AND DISCUSSION

Extraction of dry nitrates with HNO_3

The value of RAWSON's nitric acid extraction method was first examined.

WILLARD AND GOODSPEED[6] pointed out that the solubility of $Sr(NO_3)_2$ and $Ca(NO_3)_2$ is greatly affected by the density of the nitric acid, a density of 1.46 being most convenient. If nitric acid of density d = 1.46 is used, some quantity of $Sr(NO_3)_2$

dissolves. If, however, nitric acid of density greater than 1.46 is used, the calcium nitrate is not readily dissolved and a considerable amount is weighed as $Sr(NO_3)_2$. The separated Ca fraction however is practically free from Sr.

Preliminary experiments showed that considerable amounts of $Sr(NO_3)_2$ are dissolved together with the $Ca(NO_3)_2$, if the digestion was carried out in a beaker covered by a watch glass. This is obviously caused by evaporation of the nitric acid by the digestion in open vessel. However, by digesting the nitrate mixture in a desiccator, containing either nitric acid of the same density as the one used for digestion, or dry $CaCl_2$, improved results were obtained, even if the digestion was continued for several days.

Procedure

A 100 mg aliquot of a calcium/strontium mixture (as nitrates), containing ^{45}Ca as tracer, is evaporated to dryness, treated with 20 ml nitric acid (d = 1.46) and digested for one day at room temperature in a desiccator containing dry $CaCl_2$. The precipitate is transferred to a weighed glass filter, washed with 10 ml nitric acid (d = 1.46) in small portions, dried for 2 hours at 130°C and weighed. An aliquot of this precipitate is mounted for radiometric counting to determine the Ca-contamination.

In another series of experiments, containing Sr-tracer, the filtrate was assayed for Ca and analysed radiometrically for Sr-contamination, after evaporation and drying.

The results are summarized in Table I.

TABLE I

SEPARATION OF Ca AND Sr WITH NITRIC ACID, d = 1.46

Sample		*Contamination of separated fractions*		*Recovery*	
Ca mg	*Sr mg*	*Ca in $Sr(NO_3)_2$ mg*	*Sr in $Ca(NO_3)_2$ mg*	*Ca %*	*Sr %*
19.95	80.9	0.17	—	99.15	—
20.3	78.4	—	0.31	—	99.6
49.0	51.6	0.78	—	98.4	—
49.2	51.6	—	0.36	—	99.3
80.0	20.2	1.7	—	97.9	—
80.2	15.5	—	0.22	—	98.6

These results show that a quantitative separation is not obtained. The amount of $Ca(NO_3)_2$ remaining in the precipitate increases with the weight of $Ca(NO_3)_2$ in the mixture, whereas the dissolved amount of $Sr(NO_3)_2$ remains fairly constant. Accurate gravimetric results are accidentally obtained by compensation of errors.

Extraction of the dry nitrates with ether-ethyl alcohol

The separation of Ca and Sr by extraction of the dry nitrates with ether-ethyl alcohol 1 : 1 mixture, as described by FRESENIUS[2] is the method which has been most applied and is recorded in all classical handbooks of analytical chemistry.

NOLL[3] stressed the importance of traces of water in the mixtures of nitrates, as well as in the solvents, and proposed a slightly modified procedure. Preliminary gravimetric experiments confirmed the statements of NOLL and showed that reliable results are obtained with macro-amounts of 1 : 1 mixtures, if care is taken to avoid all traces of water.

Both the method of FRESENIUS and the modified procedure according to NOLL have been checked by tracer technique. Absolute alcohol and sodium dried ether were used. Extraction and filtration took place in a gloved box, containing silica gel. It appeared that NOLL's method gave slightly better results.

Procedure

A 100 mg Ca-Sr nitrate mixture is dried at 170° at constant weight. The dry mixture is pulverized and digested with 4 ml ethyl alcohol at room temperature. After 2 hours 4 ml ether are added and the digestion continued overnight. The whole process takes place in a gloved box. The strontium nitrate is finally filtered off, washed with absolute alcohol-ether mixture and dried. It is tested for Ca-contamination whereas the filtrate is analysed for Sr-contamination as above.

The results are given in Table II.

TABLE II

SEPARATION OF Ca AND Sr BY EXTRACTION WITH ETHER-ETHYL ALCOHOL

Sample		*Contamination of separated fractions*		*Recovery*	
Ca mg	*Sr mg*	*Ca in $Sr(NO_3)_2$ mg*	*Sr in $Ca(NO_3)_2$ mg*	*Ca %*	*Sr %*
19.5	75.8	0.15	—	99.25	—
20.6	81.0	—	0.19	—	99.77
50.6	52.7	0.4	—	99.21	—
50.3	52.2	—	0.5	—	99.02
80.3	21.5	0.9	—	98.9	—
77.0	22.1	—	0.9	—	95.9

From these results it appears that FRESENIUS' method, modified according to NOLL, yields no better results than RAWSON's. Owing to the simplicity of the experimental procedure the latter has to be preferred, the more that $Sr(NO_3)_2$, as stated by WILLARD AND GOODSPEED[6], and more recently by KOBE AND MOTSCH[11], forms a gelatineous precipitate in organic solvents and is less readily filtered.

Separation with isoamyl alcohol

BROWNING[4] describes the separation of Ca and Sr with isoamyl alcohol (B.P. 128°). After addition of 10 to 30 ml of solvent to a saturated aqueous solution of the nitrates, the liquid is boiled, expelling the water present. $Ca(NO_3)_2$ goes into solution whereas insoluble $Sr(NO_3)_2$ separates. Quantitative results have not yet been communicated. According to the solubility date of SEIDELL[12] isoamyl alcohol should give a better separation than most other organic reagents.

Preliminary experiments, however, have shown that a quantitative removal of the water by boiling the solution is not feasible. This causes incomplete precipitation of the strontium nitrate, and also considerable contamination of the latter with Ca occurs.

$Sr(NO_3)_2$ can be obtained in a fairly pure state after double extraction, but the quantity dissolved also increases.

The procedure is less time-consuming than the preceding ones. The filtration however is more difficult.

Experimental results are given in Table III.

TABLE III

EXTRACTION OF THE NITRATES WITH ISOAMYL ALCOHOL

Sample		*Contamination of separated fractions*		*Recovery*	
Ca mg	*Sr mg*	*Ca in $Sr(NO_3)_2$*[b] *mg*	*Sr in $Ca(NO_3)_2$*[a] *mg*	*Ca*[b] %	*Sr*[a] %
21.6	79.7	0.1	—	99.54	—
20.4	82.7	—	0.58	—	99.30
52.4	50.0	0.5	—	99.05	—
49.7	50.9	—	1.1	—	97.8
78.2	21.1	0.17	—	99.78	—
80.0	22.2	—	0.45	—	97.96

[a] after single extraction
[b] after double extraction

From these results it appears that 1 to 2% of the $Sr(NO_3)_2$ remains in the solution after one extraction, whereas 0.2 to 1% of calcium is still present in the strontium fraction after 2 extractions.

Selective precipitation of $Sr(NO_3)_2$ with HNO_3

Based on the study of the influence of the nitric acid concentration on the solubility of the Ca and Sr nitrates, WILLARD AND GOODSPEED[6] obtained a good separation of both elements from 1 : 1 mixtures by adding HNO_3, d = 1.51, to a diluted nitric acid solution, until the final density reaches a value of 1.45. Before filtration the precipitate of $Sr(NO_3)_2$ is left 1 to 2 hours in contact with the solution in a closed vessel. For less favourable ratio's of Ca : Sr double precipitation is recommended. The nitric acid should be added dropwise under vigorous stirring.

Radiochemical investigation of this method has shown that the separation is never quantitative after a single precipitation. Results communicated in Table IV show that a very pure precipitate of $Sr(NO_3)_2$ is obtained after double precipitation.

TABLE IV

SEPARATION BY SELECTIVE PRECIPITATION WITH HNO_3

Sample		*Contamination of separated fractions*		*Recovery*	
Ca mg	*Sr mg*	*Ca in $Sr(NO_3)_2$*[b] *mg*	*Sr in $Ca(NO_3)_2$*[a] *mg*	*Ca*[b] %	*Sr*[a] %
19.9	79.8	0.0012	—	99.994	—
20.6	80.9	—	0.55	—	99.32
50.3	50.3	0.007	—	99.985	—
49.8	51.5	—	1.6	—	96.9
80.2	19.9	0.045	—	99.94	—

[a] after single precipitation
[b] after double precipitation

Precipitation from homogeneous solution

A separation method based on the selective precipitation of $SrSO_4$ from homogeneous solution, using dimethyl sulfate, has been described by ELVING AND VAN ATTA[5] using the following procedure: 25 ml of a solution of the mixed nitrates, containing Ca or Sr tracer, are treated with 20 ml of methyl alcohol and 0.5 ml of

$(CH_3)_2SO_4$ for each 10 mg quantity of Sr present. After thorough mixing, the solution is heated at about 60°C. As the hydrolysis of $(CH_3)_2SO_4$ proceeds, $SrSO_4$ gradually precipitates. After about 1 hour the precipitate has settled and can be separated from the clear supernatant solution.

The results obtained are summarized in Table V, showing that the $SrSO_4$ precipitation is not quantitative if a large amount of Ca is present.

TABLE V

SEPARATION OF Ca AND Sr BY PRECIPITATION FROM HOMOGENEOUS SOLUTION

Sample		*Contamination of separated fractions*		*Recovery*	
Ca mg	*Sr mg*	*Ca in $SrSO_4$ mg*	*Sr in $CaSO_4$ mg*	*Ca %*	*Sr %*
21.5	80.2	0.4	—	98.15	—
19.0	80.9	—	0.31	—	99.62
50.2	50.4	1.5	—	97.0	—
49.8	50.6	—	0.5	—	99.01
79.8	20.6	0.6	—	99.25	—
79.6	22.5	—	1.3	—	94.25

The influence of the amount of added reagent has been investigated in a special series of experiments. Solutions containing 20 mg of Sr and 80 mg of Ca were treated respectively with 1, 2 and 5 ml reagent. In each case the amount of Sr remaining in the solution and the amount of $CaSO_4$ coprecipitated with the $SrSO_4$ were determined by radiochemical techniques. The results are represented in Fig. 1.

It is obvious that the slight excess of reagent, necessary for the quantitative precipitation of $SrSO_4$, causes considerable coprecipitation of $CaSO_4$. Hence this method cannot be recommended for the separation of Sr from Ca in mixtures of unknown composition.

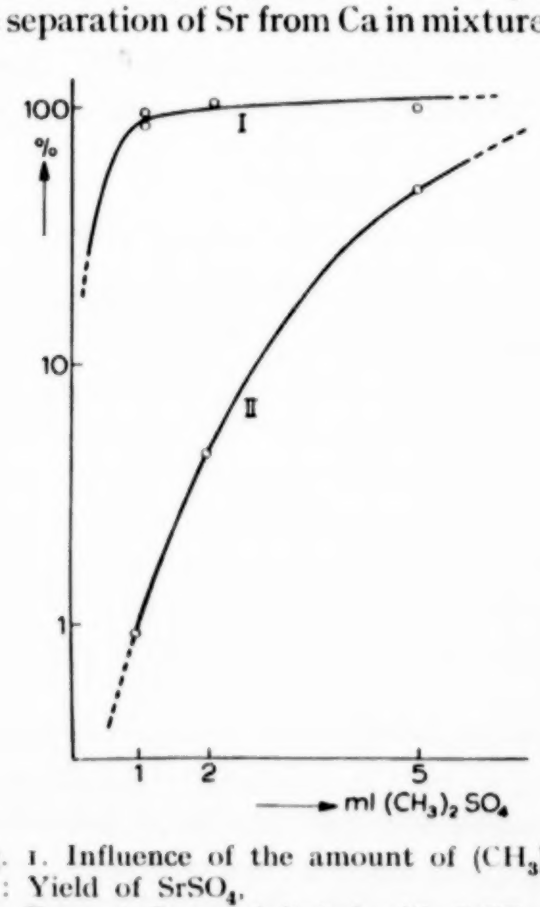

Fig. 1. Influence of the amount of $(CH_3)_2SO_4$.
I: Yield of $SrSO_4$.
II: Procent Ca precipitated with $SrSO_4$.

References p. 320

Selective precipitation of Sr as $SrCrO_4$

There is little agreement in the literature concerning the value of the chromate precipitation method for the separation of Sr and Ca. DAVIS[9] states that, on account of solubility data, a good separation should be obtained, whereas FRESENIUS AND RUPPERT[7] found experimentally unreliable results.

The method is based on the insolubility of $SrCrO_4$ in aqueous alcoholic solution. The solution of the Sr-Ca mixture is treated with K_2CrO_4, heated at 60°C, and ethyl alcohol is added for precipitation of $SrCrO_4$. FRESENIUS AND RUPPERT added one half the volume of the solution. DAVIS on the other hand added an equal volume of alcohol and recommends filtration of the warm solution. We have checked both procedures by radiochemical control. The results can be found in Table VI.

Our results confirm the experiences of FRESENIUS: no satisfactory separation could be achieved and the method gives only good results by accidentally compensation of the errors.

An attempt was made to obtain better results by the precipitation of $SrCrO_4$ from homogeneous solution, by adding acetone instead of ethyl alcohol to the slightly acid solution, followed by gradual neutralization with gaseous ammonia. Coprecipitation of $CaCrO_4$ could not be avoided even in these conditions.

In this connection it is doubtful whether 0.1 mg of Ca can be detected as oxalate in the filtrate of $SrCrO_4$, precipitated by addition of ethyl alcohol to the solution of mixed chromates, as stated by KOLTHOFF[8].

TABLE VI

SEPARATION OF Ca AND Sr BY PRECIPITATION OF $SrCrO_4$

Sample		*Contamination of separated fractions*		*Recovery*	
Ca mg	*Sr mg*	*Ca in $SrCrO_4$ mg*	*Sr in $CaCrO_4$ mg*	*Ca %*	*Sr %*
		Procedure of FRESENIUS-RUPPERT			
20.1	79.8	2.44	—	87.9	—
20.0	81.3	—	6.27	—	92.3
51.9	49.8	2.3	—	95.5	—
50.5	51.1	—	4.1	—	92.0
80.9	20.1	1.4	—	98.3	—
80.0	21.4	—	4.1	—	81.0
		Procedure of DAVIS			
19.3	83.2	0.6	—	96.7	—
19.7	82.8	—	23.2	—	72.0
50.9	50.4	0.75	—	98.5	—
50.8	51.6	—	8.7	—	83.1
80.3	24.5	2.3	—	97.1	—
81.3	21.7	—	0.9	—	95.8

CONCLUSIONS

Among all the methods investigated the extraction with HNO_3 according to RAWSON[1] or with an ethyl alcohol-ether mixture according to FRESENIUS[2] gives the most reliable results, although both methods give no quantitative separation. Hence the percentage error increases when the concentration ratio becomes less favourable.

It was found that a very pure $Sr(NO_3)_2$ fraction can be obtained by double precipitation with conc. HNO_3, according to WILLARD AND GOODSPEED[6].

Besides, it could be established that the extraction of the dry nitrates with HNO_3 of density $d > 1.46$ gives a $Ca(NO_3)_2$ fraction, practically free from Sr. These results have been used for the development of a new method.

DETERMINATION OF Sr AND Ca IN MIXTURES BY THE ISOTOPIC DILUTION METHOD

The isotopic dilution method is based on the fact that, when a radiotracer is added to a solution of its not active isotope, present in the same chemical form, the ratio of active and stable isotope in the precipitate formed by adding a suitable reagent to the solution is equal to their ratio in the solution before precipitation. It can be derived, when no active isotope is present in the original solution, that the weight G_x of the element sought is given by the relation:

$$G_x = G_d \left(\frac{S_d}{S_{exp.}} - 1 \right)$$

where: G_d: weight of tracer added
S_d: specific activity of tracer added
$S_{exp.}$: specific activity of isolated precipitate

The method involves the isolation of the element to be determined with a high degree of purity. Precipitation however ought not to be quantitative.

Conditions for the determination of Sr

It was found that a fairly pure $Sr(NO_3)_2$ can be obtained by double precipitation with concentrated HNO_3.

Solubility data of WILLARD AND GOODSPEED[6] show that the density of HNO_3 shall be less than 1.46 in order to avoid coprecipitation of Ca.

Although a quantitative precipitation is not necessary, a good yield can be desirable, especially when small amounts of Sr are to be determined. Therefore, the influence of the precipitation speed on the yield and the purity of the precipitated $Sr(NO_3)_2$ has been examined. The less favourable ratio Sr : Ca = 20 mg : 80 mg has been used in these experiments, and HNO_3, $d = 1.53$, has been added until the density reached the value $d = 1.45$. Final volume has been reduced to 30 ml in order to be able to apply the method to the determination of small quantities of Sr. In these conditions however some $Ca(NO_3)_2$ is precipitated with the $Sr(NO_3)_2$.

The results are represented in Fig. 2.

It can easily be seen that the time for precipitation should be at least 30 minutes.

Conditions for the determination of Ca

It has already been mentioned that practically no $Sr(NO_3)_2$ dissolves in HNO_3 of density > 1.46 and a pure $Ca(NO_3)_2$ fraction can be obtained in this way, although the separation is not quantitative.

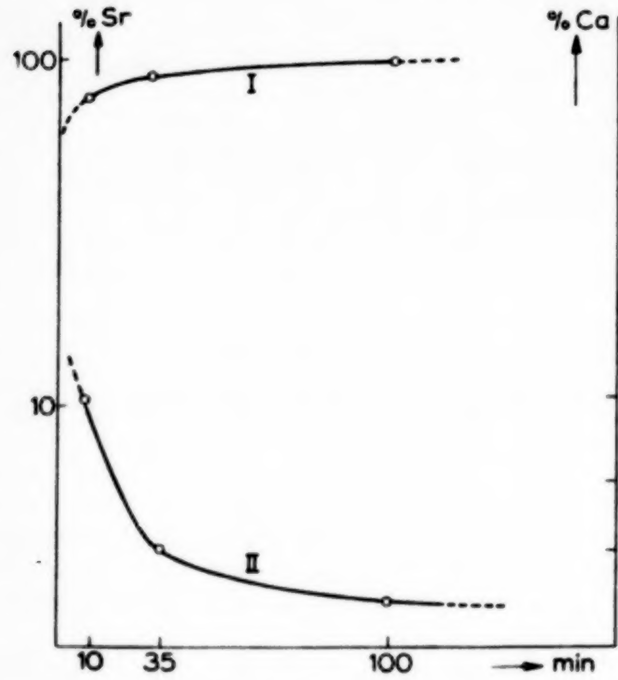

Fig. 2. Influence of the precipitation time.
I: Yield of $Sr(NO_3)_2$.
II: %Ca precipitated with $Sr(NO_3)_2$.

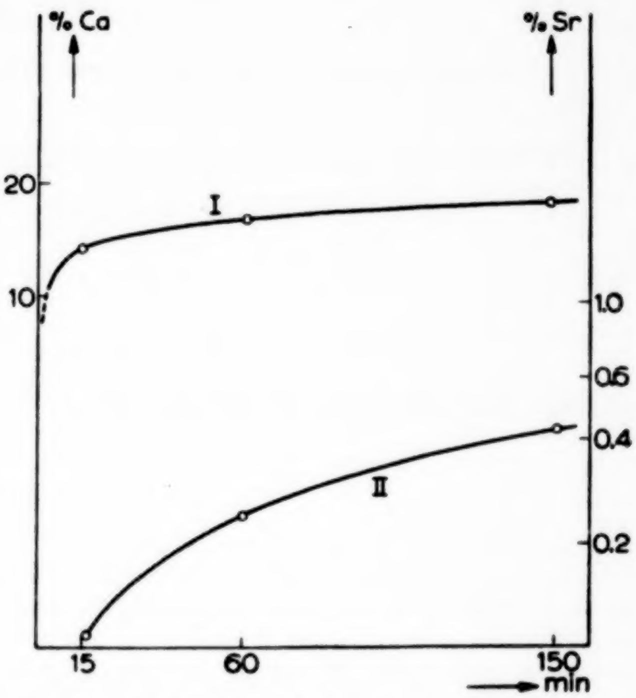

Fig. 3. Influence of the extraction time.
I: Yield of $Ca(NO_3)_2$.
II: Procent Sr dissolved.

Experiments were drawn in order to determine the influence of the extraction time on the yield and the purity of the $Ca(NO_3)_2$ obtained, using HNO_3, d = 1.468. The results obtained for the less favourable ratio Ca : Sr = 20 mg : 80 mg are drawn in Fig. 3.

It is obvious that the best results are obtained when the extraction time is short. Extraction for 15 min is to be recommended.

Procedure and results

Based on the above experiments the following procedure has been adopted: To a neutral mixture of calcium and strontium nitrates, a known amount of tracer Sr and Ca is added. After homogeneisation, HNO_3, d = 1.51, is added dropwise under vigorous stirring until the final density reaches the value, d = 1.45, this taking about 30 to 40 minutes. The $Sr(NO_3)_2$ precipitate is filtered off, redissolved and purified by double precipitation. The pure precipitate is filtered, washed with HNO_3, d = 1.45, dried at 135°, and weighed as strontium nitrate. The filtrate is evaporated to dryness. The residue is digested with 10 ml HNO_3, d = 1.468, for 15 min and filtered. The filtrate, containing pure $Ca(NO_3)_2$ is evaporated to dryness in the presence of an excess of sulfuric acid and the residue is weighed as $CaSO_4$. From the activities of a known weight of each pure fraction, and of the pure tracer added, specific activities can be computed and the percentage of Sr and Ca can be calculated with the above formula.

The procedure has been checked on a semi-micro scale with Ca-Sr mixtures 1 : 1 of total metal content of about 20 mg, weights being determined on the microbalance. Owing to the small weights of samples correction for self-absorption could be avoided when the measured weights of precipitate and of tracer were nearly equal.

The results obtained by this method are shown in Table VII.

It can be seen that the accuracy obtained with 20 mg samples is comparable with that obtained by the best gravimetric methods with 100 mg samples.

TABLE VII

DETERMINATION OF Ca AND Sr IN MIXTURES BY THE ISOTOPIC DILUTION METHOD

Sample	*mg present*		*mg found*		*% error*	
	Sr	*Ca*	*Sr*	*Ca*	*Sr*	*Ca*
I	4.89	4.12	5.05	4.23	+3.2	+2.6
II	5.025	4.18	5.145	4.34	+2.4	+3.6

The authors wish to thank Dr J. HOSTE for the correction of the manuscript.

SUMMARY

The quantitative separation of Ca and Sr by some of the most interesting chemical procedures has been investigated, using radiochemical tracer techniques. It could be shown that no satisfactory separation could be achieved and good results are obtained in some cases by compensation of errors.

The results have been used for the development of an isotopic dilution method for the determination of Ca and Sr in mixtures of their salts. Reliable results are obtained on the semi-microscale.

RÉSUMÉ

La séparation du calcium et du strontium par quelques-unes des méthodes chimiques les plus intéressantes a été étudiée au moyen des traceurs ^{45}Ca et ^{89}Sr. Il s'est avéré qu'aucune méthode ne permet d'obtenir une séparation quantitative, mais qu'on obtient souvent des résultats satisfaisants par compensation des erreurs.

Les résultats ont permis d'établir une nouvelle méthode par dilution isotopique pour la détermination des deux éléments dans un mélange de leurs sels. Des résultats satisfaisants ont été obtenus à l'échelle semi-micro.

ZUSAMMENFASSUNG

Einige der gebräuchlichsten chemischen Methoden zur Trennung von Calcium und Strontium wurden mit Hilfe der Isotopen ^{45}Ca und ^{89}Sr untersucht. Es zeigte sich dass eine quantitative Trennung niemals erfolgt und gute gravimetrische Resultate vielleicht durch Fehlerkompensation zu erklären sind.

Die Ergebnisse dieser Experimente erlaubten die Entwicklung einer Isotopenverdünnungsmethode für die Bestimmung von Ca und Sr in ihren Salzgemischen. Im Semimikro-Bereich wurden befriedigende Resultate erhalten.

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A HETEROMETRIC MICRO-DETERMINATION OF LEAD WITH SODIUM DIETHYLDITHIOCARBAMATE

by

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INTRODUCTION

No gravimetric macro or micro method for the determination of lead with sodium diethyldithiocarbamate (= CBM) appears to exist. A heterometric method for determining traces of lead in aqueous solutions which may contain large excesses of foreign metals is presented here. The solution to be analysed may contain 0.02-0.04 mg lead per ml of solution and a complete titration takes 8-15 minutes at room temperature. The error is generally less than 1%. The determination can be made successfully in solutions which contain $\geqslant$ 99.5% of the following cations: Ca^{+2}, Sr^{+2}, Ba^{+2}, Mg^{+2}, Zn^{+2}, Mn^{+2}, Ni^{+2}, Al^{+3}, Cr^{+3}, Cd^{+2}, Cu^{+2}, Sb^{+3}, Hg^{+2} and Ag^{+}. Only in the presence of Fe^{+3} or Co^{+2} is the percentage of lead relative to the foreign metal somewhat higher.

In order to save space only a small part of the experiments carried out are reported here. In each case the composition of the analysed solution and the working condition, in a final form, are presented.

EXPERIMENTAL

Instrumentation. A "Heterometer" designed by one of us (M.B) was used[1-2]. The titrated solution was thermostatically controlled at 20°C. Although a controlled temperature was generally unnecessary, it was maintained here in order to obtain maximum optical density values which could be compared one with another. For the same reason the rate of stirring was electronically controlled and was more or less constant in all titrations. The rate of stirring was generally the maximum consistent with stabie galvanometer readings. The measurements were subject to an uncertainty of ± 0.001 microamperes. Constant readings were generally obtained in a few seconds.

Reagents. The sodium diethyldithiocarbamate (= CBM) was a Fisher reagent. A stock solution was prepared and was stored in a dark brown bottle. The solution was stable for several months. The diluted solutions were freshly prepared every few days. The titre of these solutions was checked with a standard copper sulphate solution. The lead nitrate was a May and Baker c.p. reagent. All the other reagents were either AnalaR or chemically pure.

Method

General. The solution to be analysed should contain 0.02-0.04 mg lead per ml of solution ($\sim 1.5 \cdot 10^{-4} M$). The determination of lead can be carried out with equal success in mineral acid, acetic acid, sodium acetate, ammoniacal citrate or tartrate solution. In all cases a horizontal maximum optical density line is obtained after the first maximum point. The latter is determined by the intersection of the last part of the titration line with the horizontal line (Fig. 1).

20 ml of solution containing 0.3-0.7 mg lead and in addition (1) 1-3 ml M nitric acid, or (2) 0.5 ml concentrated NH_3 + 1-10 ml M Na_3-citrate or M K_2-tartrate, or (3) 1-10 ml M Na-acetate, are titrated with a 0.001-0.002M CBM.

TABLE I Composition: 5 ml 0.000666M $Pb(NO_3)_2$ + *a* ml supplements + (15-*a*) ml H_2O + *x* ml 0.001623M CBM. Lead concentration 0.000166M, 0.000083M; lead content 0.6907 mg, 0.3453 mg; calculated x = 4.08 ml. Temp. 20°C

Exp. no.	*Supplements*	*% Pb*	*End-point x ml found*	*Initial precip. at ml*	*Maxim. density value*	*Titration time in min*	*% error*
1	1 ml M HNO_3		4.04	0.4	0.50	11	1.0
2	3 ,, ,, ,,		4.08	0.4	0.51	11	0.0
3	* 3 ,, ,, ,,		4.10	0.2	0.40	15	0.5
4	3 ,, ,, CH_3COOH		4.10	0.4	0.52	11	0.5
5	5 ,, ,, H_3PO_4		4.08	0.4	0.49	16	0.0
6	3 ,, ,, CH_3COONa		4.12	0.4	0.40	10	1.0
7	1 ,, ,, ,, + 5 ml M K_2-tartrate		4.12	0.4	0.27	11	1.0
8	1 ,, ,, ,, + 5 ,, ,, Na_3-citrate		4.10	0.4	0.30	12	0.5
9	1 ,, ,, ,, + 5 ,, ,, citric acid		4.07	0.4	0.47	11	0.2
10	0.5 ,, conc. NH_3 + 5 ,, ,, Na_3-citrate		4.06	0.6	0.46	8	0.5
11	0.5 ,, ,, ,, + 5 ,, ,, K_2-tartrate		4.12	0.8	0.49	15	1.0
12	3 ,, M CH_3COONa + 6 ,, 3M KCN		4.10	0.2	0.45	15	0.5
13	3 ,, ,, CH_3COOH + 5 ,, 0.2 M Na_2H_2EDTA		4.10	1.0	0.15	14	0.5
14	3 ,, ,, HNO_3 + 10 ,, M $MgCl_2$	0.28	4.08	0.4	0.55	12	0.0
15	3 ,, ,, ,, + 10 ,, ,, $Ca(NO_3)_2$	0.18	4.05	0.4	0.44	13	0.7
16	3 ,, ,, ,, + 10 ,, ,, $BaCl_2$	0.05	4.05	0.6	0.41	15	0.7
17	1 ,, ,, CH_3COONa + 12 ,, 3M KCN + 2 ml 2M $Zn(NO_3)_2$	0.27	4.04	0.2	0.50	9	1.0
18	1 ,, 2M ,, + 12 ,, 3M ,, + 2 ,, M $MnCl_2$	0.64	4.07	0.4	0.54	8	0.2
19	0.5 ,, conc. NH_3 + 10 ,, M Na_3-citrate + 2.5 ml 2M $MnCl_2$	0.25	4.08	0.4	0.35	10	0.0
20	1 ,, M CH_3COONa + 9 3M KCN + 5 ml M $Ni(NO_3)_2$	0.24	4.05	0.2	0.48	9	0.7
21	0.5 ,, conc. NH_3 + 3 ,, M Na_3-citrate + 1 ml 0.1M $Co(NO_3)_2$	12.0	4.10	0.4	0.41	24	0.5
22	3 ,, M HNO_3 + 5 ,, ,, $Al(NO_3)_3$	0.5	∞	0.6	∞ 0.37	10	
23	6 ,, ,, ,, + 5 ,, ,, ,,		∞	0.6	∞ 0.41	10	
24	2 ,, ,, ,, + 3 ,, ,, ,,	0.9	4.10	0.4	0.47	12	0.5
25	5 ,, 2M CH_3COONa + 5 ,, ,, ,,	0.5	4.06	0.4	0.52	9	0.5
26	4 ,, 5M ,, + 10 ,, ,, ,,	0.26	4.10	0.4	0.46	11	0.5
27	3 ,, M HNO_3 + 3 ,, ,, $Cr(NO_3)_3$	0.45	4.08	0.2	0.39	11	0.0
28	2 ,, ,, NH_3 + 12 .8 ml 0.125M $Na_4P_2O_7$ + 0.2 ml M $FeCl_3$	6.3	4.04	0.6	0.36	23	1.0
29	10 ,, 0.25M $Na_5P_3O_{10}$ + 0.5 ml M $Fe(NO_3)_3$	2.5	4.10	0.6	0.34	8	0.5
30	1 ,, 2M CH_3COONa + 9 ml 3M KCN + 5 ml M $Cd(NO_3)_2$	0.12	4.05	0.2	0.44	8	0.7
31	1 ,, M ,, + 9 ,, 3M ,, + 5 ,, ,, $Cu(NO_3)_2$	0.22	4.10	0.4	0.30	20	0.5
32	1 ,, 2M ,, + 6 ,, 3M ,, + 3 ,, ,, ,,	0.37	4.02	0.4	0.32	15	1.5
33	1.5 ,, conc. NH_3 + 6 ml M K_2-tartrate + 2 ml 2M $MgCl_2$ + 5 ml 0.4M $SbCl_3$ (in 2M HCl)	0.29	4.10	0.4	0.38	10	0.5
34	1.5 ,, ,, ,, + 6 ml M K_2-tartrate + 2 ml 2M NH_4Cl + 5 ml 0.4M $SbCl_3$ (in 2M HCl)		4.10	0.4	0.36	11	0.5
35	3 ,, M CH_3COONa + 6 ml 3M KCN + 6 ml 0.2M $Hg(NO_3)_2$ (+ HNO_3)	0.29	4.10	0.0	0.60	10	0.5
36	1 ,, ,, ,, + 9 ,, 3M ,, + 5 ,, M $AgNO_3$	0.13	4.05	0.4	0.54	10	0.7

CBM = Sodium diethyldithiocarbamate; EDTA = Ethylenediaminetetraacetate; * 5 ml 0.000333M Pb, 0.00081M CBM.

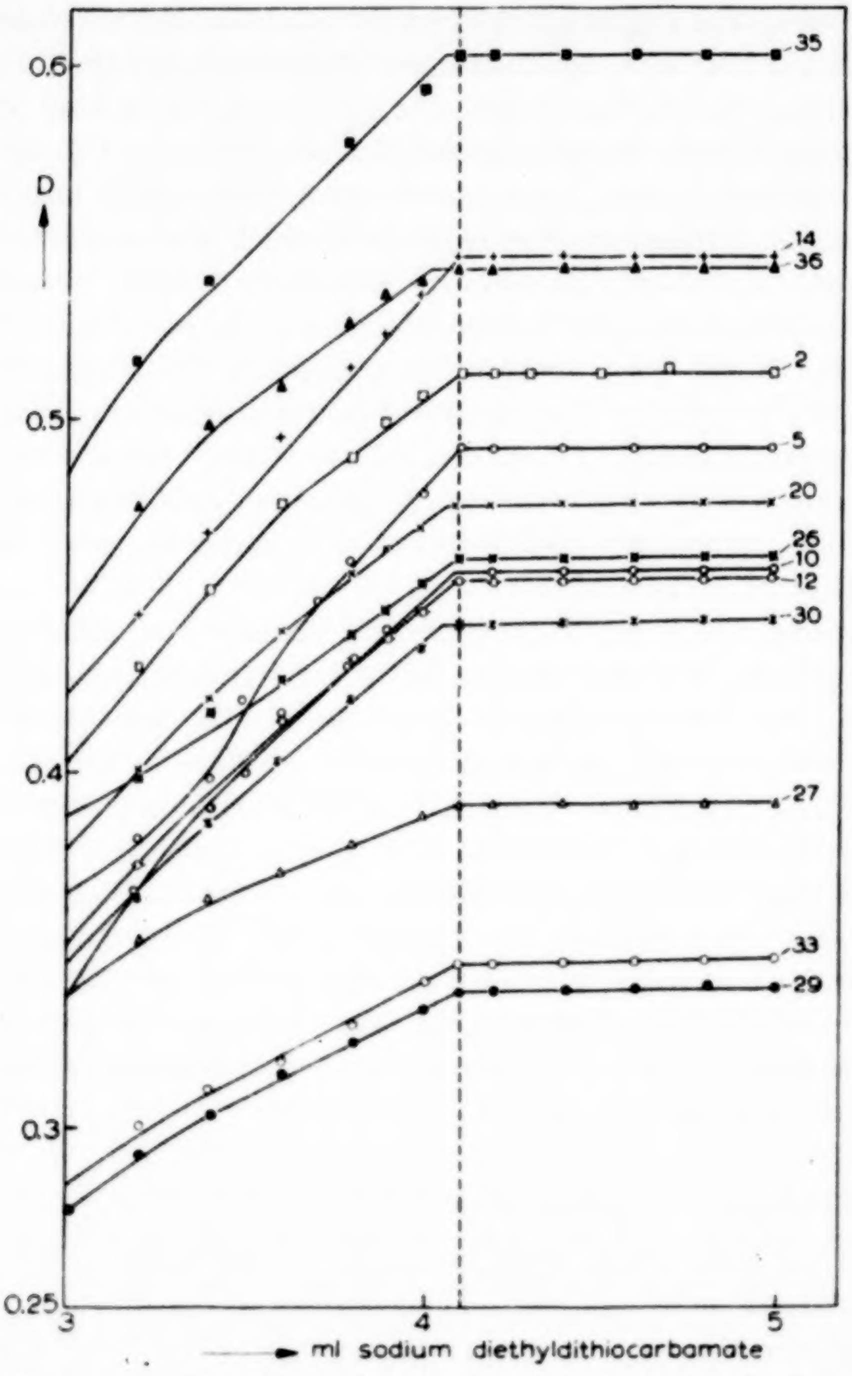

Fig. 1. Titration curves of lead nitrate with sodium diethyldithiocarbamate

RESULTS AND DISCUSSION

General aspects

The experiments and results are compiled in Table I. The course of the titration of some of them is presented in Fig. 1. From the results it may be concluded that the titration could be carried out in strong acid, in ammoniacal tartrate or citrate or in sodium acetate solutions as desired. In all cases a very fine white crystalline precipitate of $Pb(CBM)_2$ was obtained. The maximum density value and consequently the sensitivity of the reaction was independent of the pH of the solution. The same applied to the titration time; this of course depended on the number of titrations of a similar character which were carried out. In almost all cases a strictly horizontal line was obtained immediately after the first maximum point. It was found that if the stirring was continued for about ten minutes after the first maximum point was obtained, the optical density began to decrease continuously. In all cases,

References p. 326

the determination of the end-point was easily made at the intersection of the last part of the titration line with the maximum optical density line. The error was in most cases less than one percent whilst the concentration of lead was $\sim 1 \cdot 10^{-4} M$. Generally, the presence of foreign cations did not influence the sensitivity of the reaction. The following complexing agents were successfully used in this work: dipotassium tartrate or trisodium citrate, both of which were either in sodium acetate or ammoniacal solution. Large excesses of potassium cyanide were used in sodium acetate solution. In special cases (to bind ferric iron (exps. 28 and 29)), when other complexing agents failed, either sodium pyrophosphate or sodium tripolyphosphate was used successfully. Even in the presence of acetic acid solution disodium ethylenediamine tetraacetate (Na_2H_2EDTA) gave a white sol and very low maximum density values (exp. 13) and therefore it could not be used as a masking agent. In the special case of aluminium, a concentrated solution of sodium acetate could be used as complexing agent (exps. 25 and 26).

Certain titrations could not be carried out because the galvanometer readings fluctuated. Specifically, this was the case when the solution contained large amounts of antimony chloride. It was found that the values became constant when the solution contained large amounts of a neutral chloride in addition to the chosen complexing agent (exps. 33 and 34). With certain cations the maximum density value was somewhat reduced when large excesses of the cation concerned were present, even though the cation was bound by a suitable complexing agent. These reduced maximum density values did not influence the location of the end-point. Special difficulties which could not be overcome were encountered in the presence of cobalt and bismuth salts. No suitable complexing agent was found for the latter. In most cases the amount of foreign metal cited in the table, is the maximum amount which could be present to ensure reliable results.

Titrations in the absence of foreign metals

In the presence of acids. There was practically no difference in the results whether 1 or 3 ml molar acetic acid was used. The presence of 3-5 ml molar citric acid or 5 ml molar phosphoric acid (exp. 5) instead of the other acids, or of a mixture of acetic acid-sodium acetate (1 : 1) had no influence whatsoever. No proportionality between the amount of lead used and the maximum density value obtained was observed. Only in very dilute lead solutions did such a proportionality exist.

In the presence of sodium acetate in molar concentration the results were not affected.

Ammonia was only used in the presence of complexing agents. A molar solution had no influence.

In the presence of complexing agents. Trisodium citrate and dipotassium tartrate could be present in large amounts but in the absence of ammonia they caused lower density values (exps. 7 and 8).

Potassium cyanide in varying amounts could be present in a sodium acetate solution without detrimental effect (exp. 12). Na_2H_2EDTA, even in acetic acid solution, depressed the maximum density value very considerably (exp. 13).

Titrations in the presence of foreign metals

Some of these titrations were carried out in the absence of complexing agents in acid solution and others in the presence of complexing agents in sodium acetate or ammonia solution. Many results obtained are taken into consideration here though not cited in the table.

In the presence of Ca^{+2}, Sr^{+2}, Ba^{+2} and Mg^{+2}. The titrations were carried out in nitric acid solution. The results were the same whether nitrates or chlorides were employed. The concentration of these metals when present could be half molar. With magnesium, the lead made up 0.3%, while with barium it made up only 0.05% of the total. Probably the amount of foreign metal could still be increased.

In the presence of aluminium, chromium or iron. When the amount of *aluminium* was $\leqslant$ 99% a nitric acid solution could be used (exp. 24). But when greater amounts of aluminium were present in the acidic solution the density values rose above the calculated end-point (exps. 22 and 23). It was found that when a *concentrated* solution of sodium acetate was used, four times as much aluminium could be present in solution (exps. 25 and 26). The acetate evidently acts as a complexing agent and masks the aluminium. Up to 99.5% of *chromium*(III) could be present in the titrated nitric acid solution. When *ferric iron* was present in solution, even in a concentration of 0.01*M*, the determination of lead was extremely difficult and was unsuccessful except in the presence of tripoly- or pyrophosphates. In their absence, the densities were mostly reduced and rose continuously above the calculated end-point. The use of hydroxylamine or sulfite in nitric acid solution was unsuccessful. The following reagents were also tried: neutral or ammoniacal citrate or tartrate, concentrated sodium acetate and concentrated phosphoric acid. The only effective complexers were sodium pyro- or tripolyphosphate (exps. 28 and 29). In both cases the iron made up 93.7 or 97.5% of the total. Although the maximum density values were reduced, a horizontal maximum density line was obtained. A white powder was precipitated.

In the presence of zinc or manganese. In both cases, in nitric acid solution, the density rose continuously above the calculated end-point. Good results were obtained in sodium acetate solutions containing potassium cyanide (exps. 17 and 18). The specified amounts are the maximum which could be held in solution. In both cases the foreign cations made up more than 99%. A much greater amount (0.25% lead) of manganese could be held in ammoniacal citrate solution (exp. 19).

In the presence of nickel or cobalt. The determination of lead (0.24%) in *nickel* presented no difficulties when an acetate solution containing potassium cyanide was used (exp. 20). In contrast, great difficulties were encountered in determining lead in the presence of *cobalt*. Only when the amount of cobalt was less than 90% could a determination be made (exp. 21).

In the presence of cadmium or copper. Traces of lead ($\sim$ 0.1%) in *cadmium* could easily be determined in acetate solution containing potassium cyanide (exp. 30). The same conditions were necessary for the determination of traces of lead in *copper* (0.2-0.3% lead). However, the maximum density value was reduced and therefore it was advisable to use a somewhat larger amount of lead for the analysis.

In the presence of antimony(III). The experiments showed the maximum amount of antimony (99.7%) which could be held in solution by complexing with ammoniacal tartrate. The lead made up only 0.3%. Even under these conditions the readings on the galvanometer showed large fluctuations. It was found that in the presence of large amounts of chloride the readings became stable (exps. 33 and 34).

In the presence of mercury or silver. In both cases, potassium cyanide in acetate solution was used successfully. With *silver* (exps. 36), the lead made up only 0.13%. The amount of lead could probably still be reduced further. The maximum density value was normal. Under the same conditions, lead could be determined in the presence of *mercuric mercury* (99.7%). More acetate had to be added (because of the free nitric acid in solution). The maximum density was high (exp. 35).

SUMMARY

The reaction between lead and sodium diethyldithiocarbamate is studied heterometrically. The influence of the milieu, conditions of acidity and of different complexing agents, was studied. 0.02-0.04 mg lead per ml of solution can be determined either alone or in the presence of large excesses of other metals. A titration is carried out at 20°C in 8-15 minutes with an error of 0.0-1.0%. The analysed solution may contain ∿ 99.5% of the following cations: Ca^{+2}, Sr^{+2}, Ba^{+2}, Mg^{+2}, Zn^{+2}, Mn^{+2}, Ni^{+2}, Co^{+2}, Al^{+3}, Cr^{+3}, Fe^{+3}, Cd^{+2}, Cu^{+2}, Sb^{+3}, Hg^{+2}, Ag^{+}.

RÉSUMÉ

La réaction entre le plomb et le diéthyldithiocarbamate de sodium est étudiée hétérométriquement. L'influence du milieu, des conditions d'acidité et de la présence de différents réactifs complexants a été examinée. 0.02 à 0.04 mg de plomb par ml de solution peuvent être dosés, même en présence d'un grand excès d'autres métaux. Un titrage peut être effectué, à 20°C, en 8-15 minutes, avec une erreur de 0.0 à 1.0%. La solution à analyser peut renfermer ∿ 99.5% des cations suivants: Ca^{+2}, Sr^{+2}, Ba^{+2}, Mg^{+2}, Zn^{+2}, Mn^{+2}, Ni^{+2}, Co^{+2}, Al^{+3}, Cr^{+3}, Fe^{+3}, Cd^{+2}, Cu^{+2}, Sb^{+3}, Hg^{+2}, Ag^{+}.

ZUSAMMENFASSUNG

De Reaction zwischen Blei und Natriumdiäthyldithiocarbamat wurde heterometrisch studiert. Der Einfluss des Milieus, der Azidität sowie verschiedener Komplexbildner wurde studiert. 0.02-0.04 mg Blei per ml Lösung können in Abwesenheit sowie Anwesenheit grosser Überschüsse an Fremdmetallen bestimmt werden. Eine Titration dauert bei 20°C etwa 8-15 Minuten. Fehler 0-1%. Die zu analysierende Lösung kann ∿ 99.5% von folgenden Kationen enthalten: Ca^{+2}, Sr^{+2}, Ba^{+2}, Mg^{+2}, Zn^{+2}, Mn^{+2}, Ni^{+2}, Co^{+2}, Al^{+3}, Cr^{+3}, Fe^{+3}, Cd^{+2}, Cu^{+2}, Sb^{+3}, Hg^{+2}, Ag^{+}.

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COLORIMETRIC AND GRAVIMETRIC DETERMINATION OF SILICON IN TITANIUM AND TITANIUM ALLOYS

by

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Improved methods are proposed in this paper for the colorimetric and gravimetric determination of silicon in titanium and titanium alloys.

COLORIMETRIC METHOD

CODELL, CLEMENCY AND NORWITZ[1] proposed a new method for the determination of silicon in titanium and titanium alloys by means of the molybdenum blue color. The method had become recognized as the only satisfactory means for determining small amounts of silicon in titanium and titanium alloys. However, the method still left something to be desired. Experiences in this laboratory over the past two years have shown that the procedure was subject to the following errors:

1. The fluoboric acid was found to attack the glassware somewhat causing high blanks and at times erratic results. This error could be particularly serious if the solutions were filtered through the glass funnels while still warm. It is usually assumed that a large excess of boric acid will repress the following hydrolysis:

$$HBF_4 + 3H_2O \rightleftharpoons H_3BO_3 + 4HF.$$

That assumption is apparently incorrect.

2. The quantity of permanganate required to oxidize the titanous ion (as much as 5 or 6 ml of 3% potassium permanganate solution, if the titanous solution has stood for only 2 or 3 hours) was found to produce at times a greenish color that caused some interference.
3. The effect of temperature on the development of the silicomolybdate and molybdenum blue colors was critical.
4. For determining the higher ranges of silicon it was necessary to prepare a separate calibration curve. The calibration curves for both the higher and lower ranges followed Beer's law, but the slopes of the two curves were considerably different.

Elimination of sources of error

It was found that the error caused by the attack of the glassware by the fluoboric acid could be eliminated by developing the color in a plastic bottle, then diluting in a volumetric flask and filtering. Since the tartaric acid has the effect of preventing the development of the silicomolybdate color[2], silica dissolved from the glass cannot interfere once the tartaric acid had been added. It was only necessary to filter a portion of the solution in the proposed method, whereas in the previous method the entire solution was filtered.

By first oxidizing the bulk of the titanium with hydrogen peroxide and then adding a small quantity of 3% potassium permanganate solution (less than 2 ml), any error due to the potassium permanganate was eliminated.

By developing the color at a fixed temperature, variation due to temperature was eliminated. The temperature 23°C was chosen because it is the average room temperature of this laboratory. Subsequent to the completion of the investigation it was brought to the authors' attention that German investigators, JORDAN AND FISCHER[3], had also found the temperature to affect the molybdenum blue color critically in the determination of silicon in titanium and titanium alloys. Those investigators recommended that the color be developed at 25°C and that the temperature be regulated by means of a constant temperature bath.

It was found that the amount of fluoboric acid was the critical factor that affected the slope of the curve. By adding sufficient fluoboric acid to compensate for the amount eliminated when a smaller aliquot of the solution was taken, the calibration curve for the lower ranges was applicable to the determination of larger amounts of silicon.

By incorporating the above modifications into the method, increased accuracy was obtained. Also the blank was practically water-white. As judged by a survey of the literature such a blank is a rarity.

The colorimetric method for the determination of silicon in titanium and titanium alloys is recommended for the range 0.003 to 1.5%.

Reagents

Boric acid solution (4%). Add 80 g of boric acid to about 1800 ml of water contained in a 2 l pyrex bottle. Warm to about 40°C to dissolve. Cool and dilute to 2 l.

Dilute hydrofluoric acid (3 to 7). Dilute 150 ml of hydrofluoric acid (50%) to 500 ml with water in a plastic bottle.

Potassium permanganate solution (3%). Store in a plastic bottle.

Ammonium molybdate solution (5%).

Tartaric acid solution (20%).

Reducing solution. Dissolve 30 g of sodium bisulfite, 1 g of anhydrous sodium sulfite and 0.5 g of 1-amino-2-naphthol-4-sulfonic acid in about 175 ml of water and dilute to 200 ml. Filter through a No. 40 Whatman filter paper and store in a plastic bottle. Prepare fresh weekly.

Standard silicon solution (1 ml = 0.05 mg Si). Three portions of sodium metasilicate, $Na_2SiO_3 \cdot 9H_2O$, were weighed into beakers, water and sulfuric acid added and the silica dehydrated in the regular manner. 1.0000 g of $Na_2SiO_3 \cdot 9H_2O$ was found to contain 0.09706 g of silicon (the theoretical amount was 0.09873 g). 1.0303 of g the $Na_2SiO_3 \cdot 9H_2O$ was dissolved in water and diluted to 2 l in a volumetric flask. The solution was stored in a wax lined bottle.

Apparatus

A Beckman Model B Spectrophotometer was used.

Procedure

0.003 *to* 0.16% *silicon.* Transfer 0.500 g of the sample to a plastic bottle, and add 40 ml of water and 5 ml of hydrofluoric acid (3 to 7) measured from a plastic buret or carefully with a plastic graduate. Let stand until dissolved (2 or 3 hours, or overnight). Add 100 ml of boric acid solution (4%) and 50 ml of water, and then add hydrogen peroxide (30%) until the solution begins to lighten in color. Four drops of hydrogen peroxide will usually be required if the solution has stood for 2 or 3 hours, 2 or 3 drops if the solution has stood overnight, and none if the solution has stood for several days. A slight excess of hydrogen peroxide is not harmful. Add potassium permanganate solution (3%) dropwise until a permanent pink color is obtained, then 2 drops in excess. Place the plastic bottle into a 1-liter beaker containing about 500 ml of boiling water, and continue the boiling for about 90 minutes. Remove the bottle and cool the solution to 23 ± 1°C in a running water bath. Add 10 ml of ammonium molybdate solution (5%) measured with a pipet. In 10 ± 1 minutes add 5 ml of tartaric acid solution (20%) measured with a pipet, and 3 ml of reducing solution measured with a buret. The reducing solution should be added to each individual sample immediately after the addition of the tartaric acid. Let stand 20 min, transfer to a 250 ml volumetric flask and dilute to the mark. Filter a portion of the solution through a No. 42 Whatman filter paper, discarding the first 15 to 20 ml of solution. Determine the transmittance at 700 millimicrons, setting the instrument at 100 per cent transmittance with the reagent blank. The reagent blank is prepared by adding 5 ml of hydrofluoric acid (3 to 7) to 40 ml of water, and carrying the sample through the determination. Convert to per cent silicon by consulting the calibration curve.

0.16 *to* 1.5% *silicon*. Proceed as above to the point at which the solution has been heated in boiling water for 90 minutes. Place the plastic bottle in an ice bath and cool to about 15°C. Transfer the solution to a 250 ml volumetric flask, immediately dilute to the mark with water and pipet a 25 ml aliquot into the original plastic bottle. Add 4.5 ml of hydrofluoric acid (3 to 7), 90 ml of boric acid (4%) and 75 ml of water, and develop the color as before. Convert to per cent silicon by consulting the calibration curve.

Preparation of calibration curve. Transfer 0.50 g samples of titanium of low silicon content to plastic bottles. Add 0, 1, 3, 5, 7, 9, 11, 13, and 15 ml portions of standard silicon solution, and carry the samples through the procedure. Plot milligrams of silicon against logarithm of the transmittance.

GRAVIMETRIC METHOD

The gravimetric determination of silicon in titanium and titanium alloys is attended with difficulty. Perchloric, hydrochloric or nitric acids cannot be used for the dehydration, because these acids cause the precipitation of considerable titanium salts. Recently a Task Force under the chairmanship of M. J. MILES, Titanium Metals Corporation of America, found the sulfuric acid dehydration method for silicon in titanium and titanium alloys to be surprisingly inaccurate.

An investigation was undertaken to find the causes of error in the sulfuric acid dehydration method for silicon in titanium and titanium alloys. It was decided that no gravimetric method would be satisfactory for the accurate determination of small amounts of silicon in titanium and titanium alloys. Therefore efforts were devoted towards finding out why the sulfuric acid dehydration method gave inaccurate results over the range 0.3 to 5% silicon. It was found that the following were the chief reasons why the method was inaccurate over that particular range:

1. On igniting the silica precipitates, a black residue was frequently obtained. It was deduced from the phase diagram of the titanium-silicon system[4] that the black residue was Ti_5Si_3. It could not be elemental silicon[4]. Experimental evidence that the residue was Ti_5Si_3 and not a higher valence silicide is in the fact that blue solutions (titanous ion) were obtained when black silica precipitates were dissolved in hydrofluoric acid. Apparently Ti_5Si_3 is quite resistant to the action of sulfuric acid. This is in contrast to the action of sulfuric acid on a solid solution of silicon in titanium (the form in which most of the silicon would be present). The solid solution would be expected to be readily attacked to produce silicic acid.

2. The ignited silica precipitates contained occluded titanium salts of varied composition which underwent indefinite changes between the first ignition and the ignition following the treatment with hydrofluoric and sulfuric acids.

3. The glassy mass of titanium sulfate produced when the silica precipitates were treated with hydrofluoric and sulfuric acids and reignited were found to retain SO_3 with great tenacity. Obviously this can cause serious error. The fact that titanium sulfate retains SO_3 on ignition is in conformance with the observations of PIGOTT[5]. The difficulty of decomposing the titanium sulfate on heating may be caused by the fact that the titanium sulfate present would be expected to have the composition $TiO_2 \cdot SO_3$, $TiO_2 \cdot xSO_3 \cdot xH_2O$, and $TiOSO_4$ than rather $Ti(SO_4)_2$[6].

It was found that the above errors could be entirely eliminated by dehydrating with sulfuric acid, fusing the silica with sodium carbonate and then dehydrating with perchloric acid. By this means the Ti_5Si_3 was completely attacked and a pure white silica precipitate always obtained. After treatment with hydrofluoric and sulfuric acids and subsequent ignition practically no residue remained.

Subsequent to the completion of this paper it has been brought to the authors' attention that L. FLAER of U.S. Naval Proving Grounds, Dahlgren, Virginia, has developed another method for the determination of silicon in titanium and titanium alloys that seems to give satisfactory results. In this method the sample is brought into solution by fusing with sodium bisulfate in a Vycor beaker or platinum dish, and the silica then dehydrated with sulfuric acid.

The gravimetric method is recommended for the range 0.3 to 5% silicon. More than 2% silicon would not be expected to be found in commercial titanium alloys since metallurgical studies[7] have shown that titanium alloys containing more than this amount of silicon have undesirable properties.

Procedure

Weigh the sample into a 400 ml beaker. Use a 2 g sample for 0.3 to 1% silicon and a 1 g sample for 1 to 5% silicon. Add 200 ml of water and 40 ml of sulfuric acid, and heat just below the boiling point until the sample is dissolved. Add 10 ml of hydrogen peroxide (30%), evaporate to fumes of sulfuric acid and fume at moderate heat for 5 to 8 min. Remove the beaker from the hot plate immediately if the titanium shows signs of hydrolysis after a few minutes fuming. Allow to cool, and add 300 ml of water and paper pulp. Filter through a No. 41 Whatman filter paper, police the beaker and wash the precipitate with 2% sulfuric acid solution. Transfer the filter paper and precipitate to a platinum crucible, burn off the filter paper at low heat and ignite for a few minutes. Fuse with sodium carbonate, and dissolve the melt in a mixture of 150 ml of water and 40 ml of perchloric acid (70%) contained in a 400 ml beaker. Evaporate to fumes of perchloric acid and fume strongly for 15 min. Filter as before, and ignite at 1100°C for 30 min. Weigh and treat with 5 ml of hydrofluoric acid (48%) and 2 drops of sulfuric acid. Evaporate to dryness on the hot plate, and ignite at 1100°C for 10 min. Weigh again. The difference in weight is silicon dioxide. The factor for converting silicon dioxide to silicon is 0.4672.

RESULTS

When the original colorimetric method was developed no titanium samples of varying silicon content were available. Now several such samples are available and their silicon content is presently being determined by a Task Force sponsored by Watertown Arsenal. The results obtained by the authors on these samples, using the proposed methods, are shown in Table I. The results show good precision. The colorimetric and gravimetric results for sample WA-42 are in satisfactory agreement. Sample WA-42 was the only sample that was within the range of both the colorimetric and gravimetric methods.

References p. 332

TABLE I

RESULTS BY PROPOSED PROCEDURES

	WA-42	*WA-43*	*WA-10*	*WA-12*	*WA-54*	*531*	*NBS 173*[a]
Colorimetric results (%)	0.40	—	0.005	0.038	0.038	0.007	0.036
	0.42		0.005	0.040	0.037	0.008	0.039
	0.41						0.038
	0.42						0.036
							0.035
							0.035
							0.035
Gravimetric results (%)	0.41	1.94	—	—	—	—	—
	0.41	1.94					
	0.42	1.95					
	0.42	1.95					

[a] National Bureau of Standards sample.

SUMMARY

Improved colorimetric and gravimetric methods are proposed for the determination of silicon in titanium and titanium alloys. In the colorimetric method the sample is dissolved in hydrofluoric acid, boric acid added and the titanium oxidized with hydrogen peroxide and permanganate. The bulk of the titanium is precipitated as a crystalline precipitate by heating in boiling water, and the molybdenum color developed. A portion of the solution is filtered and the transmittance measured. In the gravimetric method the sample is fumed with sulfuric acid, the silica ignited and fused with sodium carbonate. The silica is then dehydrated with perchloric acid. The colorimetric method is recommended for 0.003 to 1.5% silicon, and the gravimetric method for 0.3 to 5% silicon.

RÉSUMÉ

Une méthode colorimétrique et une méthode gravimétrique sont proposées pour le dosage du silicium dans le titane et ses alliages. Dans le procédé colorimétrique, l'échantillon est attaqué par l'acide fluorhydrique; on ajoute de l'acide borique; le titane est ensuite oxydé par le peroxyde d'hydrogène et le permanganate. La majeure partie au titane est précipitée à l'état cristallin par chauffage dans l'eau bouillante et la coloration du bleu de molybdène est developpée. On filtre une partie de la solution et on mesure l'absorption. Dans le procédé gravimétrique, l'échantillon est évaporé avec de l'acide sulfurique jusqu'à formation de fumées blanches; la silice formée est ensuite calcinée et fondue avec du carbonate de sodium. La silice est alors deshydratée par l'acide perchlorique. La méthode colorimétrique est recommandée pour des teneurs en silicium de 0.003 à 1.5% et la méthode gravimétrique pour des teneurs de 0.3 à 5%.

ZUSAMMENFASSUNG

Eine kolorimetrische und eine gravimetrische Methode zur Bestimmung von Silizium in Titan und Titanlegierungen werden vorgeschlagen. Bei der kolorimetrischen Methode wird die Probe in Fluorwasserstoffsäure gelöst, Borsäure zugefügt und das Titan mit Wasserstoffperoxyd und Permanganat oxydiert. Durch Erhitzen in kochendem Wasser fällt man die Hauptmenge des Titans in kristalliner Form aus. Nun entwickelt man die Farbe des Molybdänblaus. Ein Teil der Lösung wird filtriert und seine Lichtdurchlässigkeit gemessen. Bei der gravimetrischen Methode wird die Probe mit Schwefelsäure abgeraucht, das Siliziumdioxyd kalziniert und mit Natriumcarbonat geschmolzen. Das Siliziumdioxyd wird dann mit Perchlorsäure entwässert. Die kolorimetrische Methode wird für Siliziumgehalte von 0.003 bis 1.5%, die gravimetrische für Siliziumgehalte von 0.3 bis 5% empfohlen.

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UV-SPECTRA OF THE COPPER CHELATE OF QUINOLINE-8-CARBOXYLIC ACID

by

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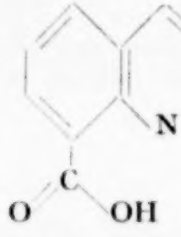
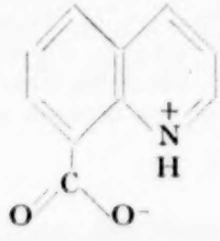
In two previous communications it has been shown by Basu and Chatterjee[1] that a comparative study of the absorption spectra of an organic legand and its metal chelate can be used effectively in getting an insight into the structure of a metal chelate. In order to give a further demonstration of the applicability of the method, we report the result of our measurement of the absorption spectra of the copper chelate of quinoline-8-carboxylic acid.

Quinoline-8-carboxylic acid (I) is amphoteric and in solution may exist as a zwitterion (II). In acid solution it should exist as (III) and in alkaline solution as (IV).



I



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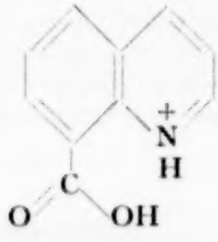

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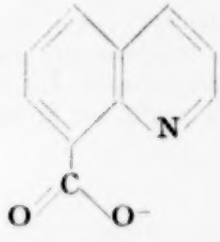

IV

In 95% ethyl alcoholic solution quinoline-8-carboxylic acid shows two absorption maxima at 295 mμ and 320 mμ respectively. In 0.1M alcoholic KOH the absorption band at 320 mμ disappears, while in 0.1M alcoholic perchloric acid only one characteristic band appears at 315 mμ. This evidently lends support to the zwitterion structure of quinoline-8-carboxylic acid.

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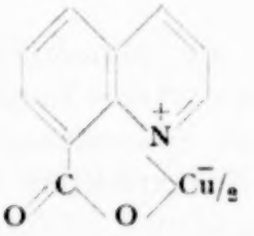
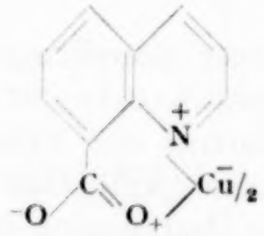
[1] S. Basu and K. K. Chatterjee, *Naturwissenschaften*, 42 (1955) 413; 43 (1956) 124.

The structure of the copper chelate of quinoline-8-carboxylic acid may be written as (V), that is the structure which is similar to that of quinoline-8-carboxylic acid in perchloric acid solution with positive charge on the nitrogen atom. In fact the chelate shows one absorption band with a sharp maximum at 320 mμ. In addition, however, there is one absorption band with a maximum at 305 mμ similar to the characteristic band in the alkaline solution of the legand. In alkaline solution, the absorption band is undoubtedly due to the carboxylate ion, and its occurrence in the chelate may indicate the ionic nature of the bond. In that case the occurrence of the 320 mμ band cannot be accounted for. Further, although the carboxylate ion band in the chelate is similar to that of the legand in alkaline solution, their positions are not exactly the same. The band in the former has a maximum at 305 mμ, while that in the latter has one at 295 mμ. If structure (VI) is considered for the chelate, it clearly shows why both these bands should appear in the chelate with their positions slightly displaced.



V



VI

Absorption spectra measurements were done in a Beckman spectrophotometer model DU, using a 1 cm quartz absorption cell. The alcohol used was refluxed over solid caustic soda and distilled. It showed complete transmission down to 220 mμ. Since the chelate did not go into true solution in cyclohexane, absorption spectra could not be measured in a non-polar solvent. The structure (VI) suggested for the chelate shows why its solubility in non-polar solvents should be low.

SUMMARY

A comparative study of the absorption spectra of an alcoholic solution of quinoline-8-carboxylic acid, with and without NaOH and perchloric acid, and its copper chelates has been made and a probable electronic structure for the metal chelates of quinoline-8-carboxylic acid has been suggested.

RÉSUMÉ

Une étude comparative a été effectuée sur les spectres d'absorption obtenus avec une solution alcoolique d'acide quinoléine-8-carboxylique (en présence et en l'absence d'hydroxyde de sodium et d'acide perchlorique) et avec ses chélates de cuivre. Une structure électronique probable est proposée pour les chélates métalliques de l'acide quinoléine-8-carboxylique.

ZUSAMMENFASSUNG

Eine vergleichende Untersuchung der Absorptionsspektren einer alkoholischen Chinolin-8-carbonsäure-Lösung (mit und ohne NaOH und Perchlorsäure) und deren Kupferchelaten wurde ausgeführt. Eine wahrscheinliche elektronische Struktur der Metallchelate von Chinolin-8-carbonsäure wurde vorgeschlagen.

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ÜBER DIE VERTEILUNG VON METALL-8-OXYCHINOLINVERBINDUNGEN ZWISCHEN WASSER UND ORGANISCHEN LÖSUNGSMITTELN

2. MITT. UNTERSUCHUNGEN ÜBER 8-OXYCHINOLIN UND SCANDIUMOXINAT IM SYSTEM WASSER-BENZOL[1]

von

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Zur Isolierung kleiner Scandiumgehalte aus Mineralien, Kohleaschen u. dgl. benutzten FISCHER, STEINHAUSER UND HOHMANN[2] eine Kombination der Fällung von Scandiumammoniumtartrat mit Yttrium als Spurenfänger und nachfolgender — unter diesen Umständen spezifischer — Ätherextraktion des Scandiums als Rhodanid. Die eigentliche Bestimmung des Scandiums erfolgte anschliessend nach erneuter Scandiumammoniumtartratfällung indirekt durch cerimetrische Titration des Tartrates im Mikromaßstab. Diese Mikrobestimmung weist bei Sc-Mengen von 30-40 γ einen Fehler von etwa 20% auf, wie bereits FISCHER und Mitarbeiter angaben und wir bestätigen konnten.

Da eine spezifische Reaktion des Scandiums bisher nicht bekannt geworden ist, die seine unmittelbare Bestimmung in Gemischen einwandfrei ermöglichen würde, wird man auf eine vorhergehende Isolierung des Scandiums nicht verzichten können. Es würde aber bereits einen Fortschritt bedeuten, wenn es gelänge, die nicht stöchiometrisch verlaufende Mikrotitration durch ein einfacher zu handhabendes und evtl. genaueres photometrisches Verfahren zu ersetzen. Folgende Überlegungen führten uns zu der Ansicht, daß das Scandium-8-Oxychinolat (kurz Scandiumoxinat genannt) eine hierfür geeignete Verbindung sei:

1. Auf Grund des sonstigen chemischen Verhaltens des Scandiums war anzunehmen, daß sich sein Oxinat dem des Aluminiums[3], oder denen der Seltenen Erden, bzw. dem des Thoriums ähnlich verhalten würde. Betreffs der Verteilung des Oxinates konnte man deshalb hoffen, zumindest im alkalischen Bereich, etwa bei pH 9-11 ein Gebiet quantitativer Extrahierbarkeit zu finden.

2. POKRAS, KILPATRICK UND BERNAYS[4] lösten festes Scandiumoxinat in Toluol und fanden ein Absorptionsmaximum in einem Wellenlängenbereich, in dem freies 8-Oxychinolin (kurz Oxin genannt) nicht merklich adsorbiert, so daß eine direkte photometrische Bestimmung auch bei einem Überschuß von Oxin möglich sein würde. Allerdings führen die genannten Autoren an, daß für die Scandiumoxinatlösungen in Toluol nicht das Beer'sche Gesetz gilt. Wir vermuteten jedoch, daß die Ursache hierfür in Dissoziations- bzw. Hydrolyseerscheinungen liegt, die sich vielleicht durch Anwendung eines genügend grossen Überschusses an freiem Oxin zurückdrängen bzw. ausschalten lassen würden. Bereits STEINHAUSER[2,5] hatte eine grosse Hydrolyseempfindlichkeit des Scandiumoxinates festgestellt: Er hatte versucht, ge-

Literatur S. 345

fälltes Scandiumoxinat mit organischen Lösungsmitteln vom Filter zu lösen, um es dann, nach Diazotierung des Oxins, colorimetrisch zu bestimmen. Diese Versuche scheiterten daran, daß es nicht gelang, gefälltes Scandiumoxinat durch Auswaschen von überschüssigem, freiem Oxin zu befreien; vielmehr verblieb dabei praktisch reines Scandiumhydroxyd auf dem Filter.

Wir prüften zunächst qualitativ unter gleichen Bedingungen eine Reihe organischer Lösungsmittel auf ihre Extraktionswirkung gegenüber Scandiumoxinat im pH-Bereich 9.5-10.5: Sehr intensive Färbungen der organischen Phase wurden erhalten mit Chloroform, Benzol und Methylpropylketon. Chloroform wäre für die Ausschütteltechnik von Vorteil, da es die schwerere Phase bildet und aus einem Schütteltrichter bequem abgelassen werden kann. Leider traten Trübungen in der Chloroformphase auf, die eine photometrische Bestimmung störten*. Wir führten deshalb die weiteren Untersuchungen mit Benzol durch und benutzten zum Ausschütteln graduierte 250 ml-Schüttelzylinder, aus denen zur Extinktionsmessung ein Teil der Benzolphase abgehebert wurde.

I. DIE VERTEILUNG DES FREIEN 8-OXYCHINOLINS ZWISCHEN WASSER UND BENZOL

Da weder die Verteilung des Oxins zwischen Wasser und Benzol in Abhängigkeit vom pH-Wert der wässrigen Phase, noch sein Spektrum in Benzol bekannt waren, untersuchten wir zunächst diese.

Zur Aufnahme des *Spektrums* stellten wir eine Oxin-Benzol-Lösung her unter ähnlichen Bedingungen, wie sie später bei den Verteilungsversuchen des Scandiumoxinates eingehalten wurden: 100 ml einer wässrigen $2.5 \cdot 10^{-4}$ molaren Oxinlösung vom pH-Wert 10.5 wurden mit zweimal 100 ml Benzol geschüttelt. Dadurch wurde das Oxin praktisch vollständig aus der wässrigen Phase entfernt, so daß die Konzentration in den vereinigten Benzolphasen $1.25 \cdot 10^{-4} M$ war. Ein Teil dieser Lösung wurde zur Entfernung letzter Wassertröpfchen durch ein trockenes Filter gegeben und das Spektrum mit einem Spektralphotometer [Sp. 500 der Firma Unicam] vermessen. Die Ergebnisse sind in Abb. 1, Kurve I, dargestellt. Das Oxin absorbiert erst merklich unterhalb 370 mμ und hat ein Absorptionsmaximum bei 316-317 mμ. Das entspricht den Messungen in Toluol ($\varepsilon_{\max} = 317$ mμ)[4] und in Chloroform ($\varepsilon_{\max} = 315.4$ mμ)[6].

Zur Bestimmung des *molaren dekadischen Extinktionskoeffizienten* $\varkappa_{\text{HOx}}$ führten wir weitere 10 Messungen an $0.5\text{-}1.0 \cdot 10^{-3} M$ Oxin-Benzollösungen durch, die teils unmittelbar durch Lösen von Oxin in Benzol, teils durch erschöpfende Extraktion einer wässrigen Oxinlösung mit Benzol hergestellt worden waren. Wir fanden für 317 mμ bei 20°C: $\varkappa_{\text{HOx}} = 2695\ (\pm 8)$. Der entsprechende Wert für eine Toluollösung bei 25°C wurde zu 2490 angegeben[4].

Die *Verteilung des freien Oxins* zwischen Wasser und Benzol wurde unter Verwendung verschiedener Puffergemische im pH-Bereich 2.5-12.5 untersucht.

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* Anmerkung bei der Korrektur: Wie W. HOFFMANN (vgl. auch Mitt. 3) inzwischen fand, lassen sich solche Trübungen beseitigen, wenn man der Chloroformphase unmittelbar nach ihrer Abtrennung von der wässerigen Phase etwa 5% Methanol zusetzt. Die übrigen Bedingungen für eine analytische Bestimmung des Scandiums mittels Chloroform sind die gleichen wie für das Arbeiten mit Benzol beschrieben.

Literatur S. 345

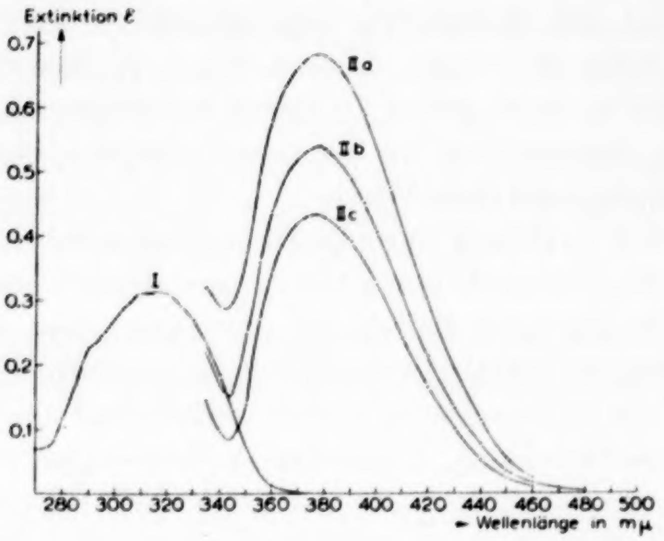

Abb. 1. Spektren von Oxin und Scandiumoxinat in Benzol (1 cm Schichtdicke)

Kurve I: 1.25 · $10^{-4}M$ Oxinlösung
Kurve IIa: 0.98 · $10^{-4}M$ Scandiumoxinatlösung
Kurve IIb: 0.78 · $10^{-4}M$ Scandiumoxinatlösung
Kurve IIc: 0.62 · $10^{-4}M$ Scandiumoxinatlösung

Zur Einstellung der gewünschten pH-Werte verwendeten wir je nach Bereich Salzsäure-Essigsäure, Essigsäure-Natriumacetat, primäres-sekundäres Natriumphosphat, Ammonchlorid-Ammoniak, Ammonchlorid-Natronlauge in der Weise, daß die Summe der einzelnen Komponenten jeweils die Konzentration 0.1N in der wässrigen Phase ergab. — Die Volumina der beiden Phasen waren gleich und betrugen je 50 ml. Das Oxin wurde in verdünnter Salzsäure oder Essigsäure gelöst und in die wässrige Phase gegeben, so daß die Konzentration daran $5 \cdot 10^{-4}M$ war. Die Bestimmung des Oxins erfolgte in der Benzolphase durch Messung der Extinktion bei 317 mμ gegen reines Benzol. Für die Aufnahme einer Eichkurve wurden bekannte Mengen Oxin direkt in Benzol gelöst. Die Extinktionsmessungen nahmen wir mit dem erwähnten Spektralphotometer vor. Zur Kontrolle der pH-Werte diente ein Röhrenvoltmeter von Hillerkus mit Glas- und Kalomelelektrode.

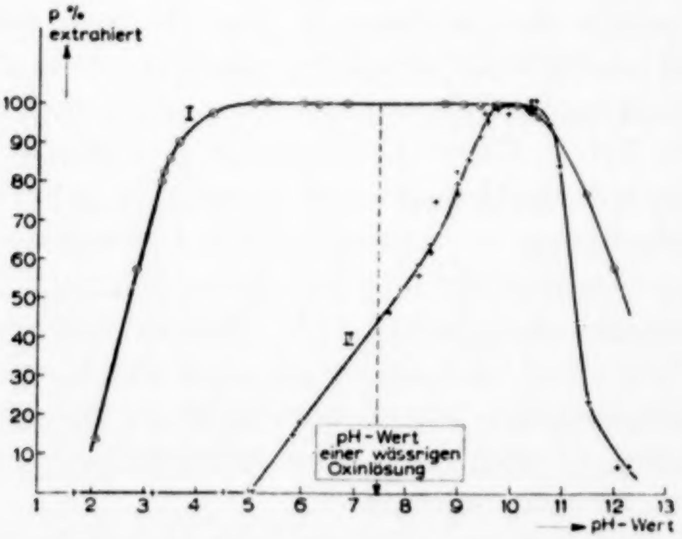

Abb. 2. Prozentische Extraktion von Oxin (Kurve I, ⊙) und Scandiumoxinat (Kurve II, +) in Abhängigkeit vom pH-Wert der wässrigen Phase.

Die Verteilungskurve des Oxins (% in der organischen Phase) in Abhängigkeit vom pH-Wert der wässrigen Phase ist in Abb. 2, Kurve I, dargestellt (ausgewählte Zahlenwerte vergl. Tab. I). Oxin wird demnach etwa zwischen pH 5-10 durch Benzol

Literatur S. 345

praktisch vollkommen extrahiert. Diese Verteilungskurve stimmt mit der von LACROIX[3] für das System Wasser-Chloroform berechneten annähernd überein, weicht aber von der für dieses System gemessenen[6] merklich ab.

Für die *mathematische Beschreibung der Verteilungsvorgänge* sind folgende Grössen von Wichtigkeit:

(Dabei stehen in eckigen Klammern die Konzentrationen [HOx] des undissoziierten Oxins, [Ox⁻] des Oxinations und [H₂Ox⁺] des Oxiniumions im Gleichgewicht. [Oxin] bedeutet Konzentration an Gesamtoxin in der Wasserschicht vor der Verteilung. Die organische und wässrige Phase sind — falls erforderlich — durch die Indices "o" und "w" unterschieden. Die elektrolytische Dissoziation in der Benzolphase wird als vernachlässigbar klein angenommen.)

Die *prozentische Verteilung* (1) $$p_{\mathrm{HOx}}\% = \frac{[\mathrm{HOx}]_\mathrm{o} \cdot 100}{[\mathrm{Oxin}]}$$

Der (*praktische*) *Verteilungskoeffizient* (2) $$K_{\mathrm{HOx}} = \frac{[\mathrm{HOx}]_\mathrm{o}}{[\mathrm{Ox}^-]_\mathrm{w} + [\mathrm{HOx}]_\mathrm{w} + [\mathrm{H_2Ox}^+]_\mathrm{w}}$$

Die beiden Grössen sind durch die Gleichungen

$$p\% = \frac{K \cdot 100}{K+1} \quad \text{bzw.} \quad K = \frac{p\%}{100 - p\%}$$

miteinander verknüpft. In Tab. I sind für einige pH-Werte die experimentell ermittelten Werte von $p\%$ und K angegeben. Zu ihrer Bestimmung wurde die nach einmaliger Verteilung in der wässrigen Phase verbliebene Oxinmenge auf zwei Wegen ermittelt: Erstens durch bromatometrische Titration und zweitens photometrisch nach nochmaliger Extraktion mit Benzol. In der Tab. I sind die Mittelwerte angegeben.

TABELLE I

VERTEILUNGSKOEFFIZIENT DES OXINS IM SYSTEM WASSER-BENZOL

pH *exper.*	$p_{HOx}\%$ *exper.*	K_{HOx} *exper.*	k_{HOx} *ber. mit unseren Diss.-Konstanten*	k_{HOx} *ber. mit den Diss.-Konstanten nach* LACROIX
2.73	50	1	(400)	230
∿7.0	99.75	∿400	424	402
9.4	99.60	247	404	340
9.8	99.37	164	425	321
12.2	50	1	(400)	240

Der *individuelle Verteilungskoeffizient* für das undissoziierte Oxin, der im Gegensatz zu K unabhängig vom pH-Wert der wässrigen Phase ist, steht damit folgendermassen im Zusammenhang:

$$(3) \quad k_{\mathrm{HOx}} = \frac{[\mathrm{HOx}]_\mathrm{o}}{[\mathrm{HOx}]_\mathrm{w}} = K_{\mathrm{HOx}} \left(\frac{D_1}{[\mathrm{H}^+]} + 1 + \frac{[\mathrm{H}^+]}{D_2} \right) \cdot$$

Darin bedeuten:

$$(4)\ D_1 = \frac{[H^+]\ [Ox^-]}{[HOx]_w} \quad \text{und} \quad (5)\ D_2 = \frac{[H^+]\ [HOx]_w}{[H_2Ox^+]}$$

Bei 50%iger Verteilung, $p\% = 50$, wird $K_{HOx} = 1$. Es gilt dann bei den entsprechenden, aus der Verteilungskurve zu entnehmenden pH-Werten 2.73 und 12.20 für

$$(3a) \qquad k_{HOx} = 1 + \frac{[H^+]}{D_2} = 1 + \frac{10^{-2.73}}{D_2} \qquad \text{und}$$

$$(3b) \qquad k_{HOx} = 1 + \frac{D_1}{[H^+]} = 1 + \frac{D_1}{10^{-12.20}}$$

Aus dem Verlauf der Kurve I in Abb. 2 kann gefolgert werden, daß nahe dem Neutralpunkt die Dissoziation des Oxins in der Wasserphase gering und in erster Näherung

$$(3c) \qquad k_{HOx} = K_{HOx} \qquad \text{ist.}$$

Setzt man nun auf Grund des bei pH 7 gefundenen K-Wertes in Gl. (3a) und (3b) $k_{HOx} = 400$, so errechnen sich die *Dissoziationskonstanten des Oxins* zu $D_1 = 10^{-9.60}$ und $D_2 = 10^{-5.33}$.

Diese für benzolgesättigte, wässrige Lösungen mit der Pufferkonzentration 0.1N geltenden Werte weichen von den von LACROIX aus Titrationskurven in reinen wäßrigen Lösungen ermittelten Werten ($D_1 = 10^{-9.82}$ und $D_2 = 10^{-5.09}$) etwas ab, führen aber zu einer besseren Konstanz der k_{HOx}-Werte bei verschiedenen pH-Werten. In Tab. 1 sind die k_{HOx}-Werte gegenübergestellt, die mittels unserer und mittels der von LACROIX angegebenen Werte für die Dissoziationskonstanten berechnet wurden.

Unabhängig von diesen Messungen läßt sich der Verteilungskoeffizient K_{HOx} bei Sättigungskonzentration aus den Werten der Löslichkeit des Oxins in den beiden Lösungsmitteln berechnen[3]. Zu diesem Zwecke ermittelten wir die *Löslichkeit des Oxins bei 18°C in Benzol,* indem wir in eine gewogene Menge Benzol portionsweise soviel Oxin eintrugen, bis nach einstündigem Rühren eine gerade sichtbare Menge Oxin ungelöst blieb. Die Dichte dieser gesättigten Lösung betrug $d_{18} = 0.927$. Mit Hilfe der bekannten Einwaagen an Benzol und Oxin errechnet sich die Löslichkeit des Oxins in Benzol bei 18° zu $l_{18} = 173$ g/l $= 1.19$ Mol/l. Die Löslichkeit des Oxins in Wasser von 18° beträgt nach LACROIX[3] 516 mg/l bzw. $3.56 \cdot 10^{-3}$Mol/l. Daraus berechnet sich angenähert der Verteilungskoeffizient des Oxins im System Wasser-Benzol zu $K_{HOx} = 334$ (entprechend einer prozentischen Verteilung von $p\% = 99.70$)bei pH 7.47, dem pH-Wert einer reinen Lösung von Oxin in Wasser. Für eine genauere Berechnung wären die Löslichkeiten des Oxins in benzolgesättigtem Wasser und in wassergesättigtem Benzol einzusetzen. — MÖLLER UND PUNDSACK[6] ermittelten für das ähnliche System Wasser-Chloroform bei 25° den Wert von $K = 353$.

Literatur S. 345

II. ANALYTISCHE UNTERSUCHUNGEN AN SCANDIUMOXINAT

POKRAS, KILPATRICK UND BERNAYS[4] fanden in einer Lösung von festem Scandiumoxinat ($ScOx_3 \cdot HOx$) in Toluol Absorptionsmaxima bei 317 und 375 mμ; das erstere deckt sich mit dem des freien Oxins. Wir fanden in benzolischer Lösung ein Maximum bei 378 mμ. Das *Absorptionsspektrum des Scandiumoxinates in Benzol* ist für drei verschiedene Scandiumkonzentrationen (0.98; 0.78 und $0.62 \cdot 10^{-4}M$) in Abb. 1 (Kurven IIa-c) dargestellt. Für das Extinktionsmaximum errechnet sich der *molare dekadische Extinktionskoeffizient* zu $\varkappa_{378} = 6900$; er liegt also höher als die von POKRAS und Mitarbeitern für Toluollösungen verschiedener Konzentration angegebenen, stark schwankenden $\varkappa_{375}$-Werte (5200-3820) und beträgt etwa das 2.5-fache des molaren dekadischen Extinktionskoeffizienten des Oxins im Absorptionsmaximum bei 317 mμ. Vergleichweise beträgt für Oxin $\varkappa_{378} = 1.4$.

Die zur Messung der Spektren benutzten Lösungen wurden hergestellt, indem je 50 ml einer $5 \cdot 10^{-5}$ molaren $ScCl_3$-Lösung, die gleichzeitig die 20-fache molare Menge Oxin enthielt und mit NH_3/NH_4Cl auf die pH-Werte 9.8, 9.0 bezw. 8.1 gepuffert war, jeweils zwei Minuten mit 25 ml Benzol geschüttelt wurden. Die Extinktionen wurden nach vorheriger Filtration der Lösungen durch ein trockenes Faltenfilter mit einem Spektralphotometer (Sp. 500 der Firma Unicam) gegen eine Vergleichslösung ohne Scandiumzusatz gemessen. — Die Konzentration des Scandiums in der organischen Phase wurde für pH 9.8 unter Zugrundelegung eines Verteilungskoeffizienten $K_{ScOx} = 65$ (siehe unten) berechnet, daraus der molare dekadische Extinktionskoeffizient ermittelt und mit dessen Hilfe die anderen Konzentrationen berechnet.

Die späteren Extinktionsmessungen erfolgten mit dem Filterphotometer ELKO II von Zeiss-Opton unter Verwendung des Filters S 38 E, das laut Angaben der Lieferfirma ein Durchlässigkeitsmaximum bei 380 mμ und eine Halbwertsbreite von 17 mμ besitzt. Bei Verwendung von Wolframlampe und Glaskondensor liegt der wirksame Filterschwerpunkt bei 387 mμ.

Der *"praktische" molare dekadische Extinktionskoeffizient* des Scandiumoxinates für das Instrument ELKO II beträgt unter diesen Bedingungen (als Mittel aus 16 Messungen) 6780(±45), weicht also nicht wesentlich von dem wahren Wert ab.

Die Verteilung des Scandiumoxinates zwischen Wasser und Benzol in Abhängigkeit vom pH-Wert der wässrigen Phase wurde unter ähnlichen Bedingungen untersucht, wie bereits für das freie Oxin beschrieben wurde.

Die wässrige Ausgangslösung wurde hergestellt durch Zusammengeben konzentrierterer Lösungen der Komponenten, so daß folgende Konzentrationen vorlagen: Sc = $10^{-4}M$, Oxin = $2 \cdot 10^{-3}M$ (Scandium:Oxin = 1:20) und Pufferlösung = 0.1*N*. Die Puffergemische — je nach pH-Bereich wurden verwendet NH_3/NH_4Cl, HCl/Borax und Essigsäure/Na-Acetat — wurden stets nach dem Oxin zugegeben, um eine Hydroxydfällung zu vermeiden. Je 25 ml dieser Lösungen wurden 2 Minuten mit 25 ml Benzol geschüttelt. Nach Trennung der Phasen wurde ein Teil der organischen Phase abgehebert, filtriert und photometriert und in der wäßrigen Phase der pH-Wert gemessen. Im Bereich hoher Extraktion (zwischen pH 9-11) schüttelten wir in einigen Fällen die von Benzoltröpfchen befreite wässrige Phase nach erneuter Oxinzugabe ein zweites Mal mit dem gleichen Volumen Benzol aus. Wie besondere Versuche zeigten, werden dabei auch die kleinen Restmengen Sc zu mehr als 90% extrahiert. Wir fanden als Mittel aus mehreren Versuchen das Extraktionsmaximum bei pH 10.2 mit $p_{ScOx}\% = 98.5(\pm 0.2)\%$ und $K_{ScOx} = 65\ (\pm 10)$. Mittels dieses $p_{ScOx}\%$-Wertes und einer bei pH 10.2 aufgenommenen Eichkurve erfolgte die quantitative Auswertung bei anderen pH-Werten.

Die Ergebnisse sind in Abb. 2, Kurve II, dargestellt, und zwar ist die von der organischen Phase extrahierte Sc-Menge in % der angewandten Menge gegen den pH-Wert der wässrigen Phase aufgetragen. Unterhalb pH 5 findet bei der angewandten Konzentration überhaupt keine Extraktion des Scandiums statt, von pH 5-9.7 ist sie unvollständig und nur in dem relativ engen Bereich von pH 9.7-10.5 ist die Lage des Verteilungsgleichgewichtes so weit zu Gunsten der organischen Phase verschoben, daß für eine analytische Bestimmung eine einmalige Extraktion ausreichend ist. Dieser pH-Bereich ist mit dem NH_3/NH_4Cl-Puffer bequem einzustellen. Da in diesem pH-Bereich eine ganze Reihe von Metalloxinaten gefärbte Benzollösungen ergeben, empfiehlt es sich, die Pufferlösung vor Verwendung durch Schütteln mit Oxin-Benzollösung zu reinigen.

Betreffs der pH-Abhängigkeit der Verteilung schließt sich Scandiumoxinat sehr nahe an die Seltenen Erden an, insbesondere ähnelt es dem Ceroxinat. Auf Grund der Zusammensetzung des festen Scandiumoxinates $ScOx_3 \cdot HOx$ ist, wie aus der Differentiation des Löslichkeitsproduktes folgt, zu erwarten, daß die Sc^{+3}-Konzentration über Sc-Oxinat als Bodenkörper in wässriger Oxinlösung einer gegebenen Gesamt-Oxin-Konzentration ein Minimum aufweist, wenn das Verhältnis Ox^--Ionen zu undissoziiertem HOx 3:1 ist. Aus unseren Dissoziationskonstanten ergibt sich, daß dieses Verhältnis bei pH 10.1 vorliegt. Da ferner im Idealfalle der Verteilungskoeffizient K einer Verbindung zwischen zwei flüssigen Phasen gleich dem Verhältnis der Löslichkeiten in beiden Phasen ist, müßte man für Scandiumoxinat ein Extraktionsmaximum bei pH 10.1 erwarten. Wie die Versuche zeigen, wird die theoretische Voraussage gut erfüllt.

Störungen bei der Extraktion des Scandiumoxinates

Bei der Anreicherungsmethode des Sc nach FISCHER und Mitarbeitern[2] können erhebliche Mengen SCN^- und SO_4^{-2} (durch Oxydation des SCN^- mit HNO_3) sowie kleine Mengen Tartrat (nach Fällung als Scandiumammoniumtartrat) in die Analysenlösung gelangen. Wir prüften deshalb besonders, in welchen Konzentrationen diese, sowie einige andere Ionen die Extraktion des Scandiums behindern können. Tabelle II gibt eine Zusammenstellung der Ergebnisse: Spalte 2 enthält die Konzentration der zugesetzten Verbindung in der wässrigen Phase; Sp. 3 die wiedergefundene Menge Sc in % des Eingesetzten (225.5 γ in 50 ml; Sc-Konz. $10^{-4}M$; Oxinkonzentration $2 \cdot 10^{-3}M$; pH 10.1-10.2; Volumen der Benzolphase 50 ml). Daraus folgt: die fraglichen Ionen SCN^- und SO_4^{-2} stören selbst bei hohen Konzentrationen noch nicht die Extraktion. Tartrat stört bei mehr als zehnfachem Überschuß, da aber im Scandiumammoniumtartrat das Molverhältnis Sc:Tartrat = 1:1 ist, sind auch nach vorhergehender Fällung keine Störungen zu erwarten.

Bei der Suche nach brauchbaren Puffergemischen fanden wir ausserdem, daß *Phosphat* die Extraktion des Scandiums verhindert. Bei Verwendung des NH_3/NH_4Cl-Puffers oder des Boratpuffers traten keine Störungen auf. Auch die Erhöhung der Pufferkonzentration auf $0.2N$ oder die Gegenwart von $0.1N$ NaCl hatte keinen Einfluß.

Die Zeitabhängigkeit der Extraktion des Scandiumoxinates

Wie bereits aus den Beobachtungen von STEINHAUSER[5] hervorging, ist das Scandiumoxinat relativ leicht hydrolysierbar. Einmal gefälltes Scandiumhydroxyd setzt sich aber beim Schütteln mit Oxinlösung nicht mit ausreichender Geschwindigkeit wieder zu Oxinat um. Um Minuswerte zu vermeiden, ist es deshalb erforderlich, das Oxin vor der Pufferzugabe in die schwach saure Scandiumsalzlösung zu geben und nach Einstellung des günstigsten pH-Wertes (10.2) das nun ausfallende Oxinat sofort mit Benzol auszuschütteln. Läßt man die Oxinatfällung längere Zeit stehen, so findet

Literatur S. 345

TABELLE II

STÖRUNGEN DER SCANDIUMOXINATEXTRAKTION DURCH ANIONEN

Zugesetztes Anion	*Konzentration (Mol/l) in der wss. Ausgangslsg.*	*% Sc wiedergefunden. Sc-Ausgangskonz. = $10^{-4}M$*
Fluorid	$2.1 \cdot 10^{-2}$	96.7
	$4.2 \cdot 10^{-2}$	72.0
	$10.6 \cdot 10^{-2}$	23.7
	$21 \cdot 10^{-2}$	0.0
Tartrat	$6.7 \cdot 10^{-5}$	100
	$6.7 \cdot 10^{-4}$	100
	$6.7 \cdot 10^{-3}$	57.2
	$2.6 \cdot 10^{-2}$	1
	$3.3 \cdot 10^{-2}$	4
Rhodanid	2.06	99
	4.12	92
	4.12	90
Cyanid	$4.0 \cdot 10^{-2}$	96.9
	$4.0 \cdot 10^{-1}$	87.5
Äthylendiamintetraacetat	$5.4 \cdot 10^{-4}$	0.0
Phosphat	0.1	0.0
Sulfat	1	100
Chlorid	0.2	100
Borat (Tetraborat)	0.1	100

man merkliche Mengen Sc zu wenig, z.B. 10% bei einstündigem Stehen. Beim Altern— oder auch bei langsamer Fällung (langsame Pufferzugabe) — erfolgt nämlich anscheinend eine Kornvergröberung des Niederschlages und damit eine Abnahme der Lösegeschwindigkeit in Benzol. Das aber begünstigt eine partielle Hydrolyse während des Verteilungsvorganges, weil der zur Stabilisierung des festen Scandiumoxinates in der wässrigen Phase erforderliche Überschuß an freiem Oxin schneller vom Benzol aufgenommen wird als die Auflösung des Oxinates erfolgt. Infolge der Reaktionsträgheit des Hydrolysenproduktes ist dieser Prozeß auch durch längeres Schütteln nicht wieder rückgängig zu machen.

Von geringerem Einfluß ist es dagegen, wenn nach dem Schütteln die organische Phase längere Zeit mit der wässrigen in Berührung steht (Extinktionsabnahme z.B. 1% in 5 Stunden).

TABELLE III

EINFLUSS DER STANDZEIT AUF DIE EXTRAHIERTE MENGE SCANDIUMOXINAT

(eingesetzt 225.5 γ Sc in 50 ml; Sc-Ausgangskonz. = $10^{-4}M$)

Standzeit des $ScOx_3 \cdot HOx$-Niederschlages vor dem Schütteln	*Standzeit der benzol. $ScOx_3$-Lösung nach dem Schütteln in Berührung mit der wss. Phase*	*% des eingesetzten Sc wiedergefunden. (Mittelwerte aus mehreren Messungen)*
1 Stunde	0	91 %
20 Stunden	0	84 %
0	10 Minuten	100.3 %
0	5 Stunden	99.4 %
0	12 Stunden	98.2 %
0	20 Stunden	93.7 %

Literatur S. 345

In Tabelle III sind die Ergebnisse solcher Versuche aufgeführt, bei denen die Standzeiten vor oder nach dem Schütteln variiert wurden.

Die besten Ergebnisse erhielt man, wenn unmittelbar nach dem Zugeben des Oxins und der Puffermischung zwei Minuten mit Benzol geschüttelt und gleich nach Trennung der Phasen (ca. 1 Minute) die Benzolphase abgenommen und zur Entfernung letzter Wassertröpfchen durch ein trockenes Filter gegeben wurde. Unter diesen Bedingungen blieb die Extinktion der Benzolphase mindestens 5 Stunden konstant. — Trocknen der organischen Phase mit wasserfreiem Natriumsulfat bewährte sich nicht, weil dabei die Extinktion der Lösung erheblich abnahm (z.B. auf 1/5 ihres ursprünglichen Wertes bei 15 Stunden Aufbewahrungsdauer über Na_2SO_4).

Der Einfluß der Oxinkonzentration auf die Extraktion des Scandiumoxinates

Wegen der grossen Hydrolysenempfindlichkeit des Scandiumoxinates ist es erforderlich, einen hohen Oxinüberschuß anzuwenden. Wir fanden, daß mindestens 20 Oxinmoleküle pro Scandiumatom bei der gewählten Sc-Konzentration ($10^{-4}M$) anwesend sein müssen, um reproduzierbare Ergebnisse zu bekommen. Wir führten zwei Versuchsserien durch, in denen einmal der Oxingehalt ($10^{-3}M$) konstant gehalten und die Scandiummenge variiert (Abb. 3), im anderen Falle bei konstanter Scandiumkonzentration ($10^{-4}M$) die Oxinmenge variiert wurde (Abb. 4). Die wässrigen Lösungen wurden mit NH_3/NH_4Cl auf pH 10.2 gepuffert und jeweils 50 ml mit 50 ml Benzol 2 Minuten geschüttelt. Die Extinktion der Benzollösung wurde nach Filtration durch ein trockenes Filter mit dem Filterphotometer ELKO II gegen reines Benzol gemessen. Sie wurde in Abb. 3 und 4 gegen die variierte Komponente der jeweiligen Versuchsreihe aufgetragen.

Zu *Abb. 3, variabler Scandiumgehalt:* Man erhält bei kleinen Scandiumkonzentrationen eine Gerade (Eichkurve!). Bei etwa 1 Sc auf 20 Oxinmoleküle biegt die Kurve um, d.h. die Extraktion des Sc ist nicht mehr vollständig. Bei etwa 1 Sc auf

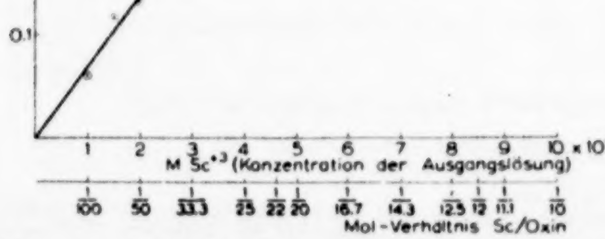

Abb. 3. Abhängigkeit der Verteilung des Scandiumoxinates von der Sc^{+3}—Konzentration der wässrigen Ausgangslösung bei konstanter Oxinkonzentration ($10^{-3}M$).
X ⟶ Fällung an der Phasengrenzfläche.
---S---Sollwert der Extinktion bei vollständiger (99%iger) Extraktion des $ScOx_3$ laut Eichkurve.

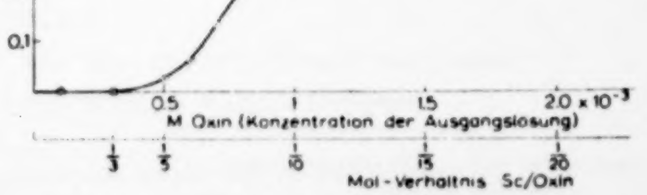

Abb. 4. Abhängigkeit der Verteilung des Scandiumoxinates von der Oxinkonzentration der wässrigen Ausgangslösung bei konstanter Sc^{+3}—Konzentration ($10^{-4}M$).
⟵ X Fällung an der Phasengrenzfläche.
---S---Sollwert der Extinktion bei vollständiger (99%iger) Extraktion des $ScOx_3$ laut Eichkurve.

Literatur S. 345

12 Oxin (in der Abbildung durch ein Kreuz gekennzeichnet) tritt ausserdem ein sichtbarer Schleier an der Phasengrenzfläche auf.

Zu *Abb. 4, variable Oxinkonzentration:* Bei weniger als 5 Molekülen Oxin pro 1 Atom Sc erfolgt praktisch überhaupt keine Extraktion; dafür tritt wieder eine Fällung an der Phasengrenzfläche auf. Von etwa 6-14 Molekülen Oxin pro Atom Sc steigt die Extinktion annähernd geradlinig mit zunehmender Oxinkonzentration. Daneben tritt immer noch eine sichtbare Fällung auf, die bei 14 Oxin gerade verschwindet (Kreuz !). Bei 20 Oxin : 1 Sc erfolgt wieder vollständige Extraktion.

Die Verteilungskurven des Scandiumoxinates, sowohl bei variablem pH-Wert (Abb. 2,II) als auch bei variablen Mengen Scandium (Abb. 3) oder Oxin (Abb. 4) lassen sich deuten durch die Überlagerung des Verteilungsgleichgewichtes des Scandiumoxinates und des Löslichkeitsgleichgewichtes eines festen Bodenkörpers. Wie in einer späteren Veröffentlichung in allgemeinerem Zusammenhange ausführlicher beschrieben werden soll, kann man aus der Form dieser Verteilungskurven Rückschlüsse auf die Zusammensetzung des Organometallkomplexes und des Bodenkörpers ziehen. Wie hier im einzelnen nicht abgeleitet sei, ergibt sich für die Verteilung des Scandiumoxinates:

1. Die stöchiometrische Zusammensetzung des gelösten Scandiumoxinates in der Benzolphase entspricht der Formel $ScOx_3$. (Vgl. den ähnlichen Befund von POKRAS UND BERNAYS[7].)
2. Der Bodenkörper bei konstantem pH-Wert, aber variablen Oxinkonzentrationen (Abb. 4), besteht mit grosser Wahrscheinlichkeit aus $Sc(OH)_3$.
3. Der Abfall der pH-Verteilungskurve (Abb. 2, II) bei hohen pH-Werten wird durch das Auftreten des gleichen Bodenkörpers bewirkt.
4. Wenn das von MOELLER UND KREMERS[8] angeführte Löslichkeitsprodukt des Scandiumhydroxyds $L_{Sc(OH)_3} = 10^{-28}$ als richtig anzusehen ist, folgt weiter aus unseren Messungen, daß das nach einmaliger Verteilung in der wäßrigen Phase verbleibende gelöste Scandium nur zu einem extrem kleinen Bruchteil aus Sc^{+3}-Ionen besteht und überwiegend als Verbindung mit OH^-, vielleicht auch Cl^- oder NH_3, vorliegt. Diese Aussage gilt auch dann noch, wenn das angegebene Löslichkeitsprodukt mit einem Fehler von 10 Zehnerpotenzen behaftet sein sollte.

Eichkurve und Prüfung auf Gültigkeit des Beer'schen Gesetzes

Wir nahmen eine Eichkurve auf mit dem Instrument ELKO II, Filter S 38 E (1 cm-Küvetten). Die Oxinkonzentration in der wässrigen Phase vor dem Schütteln war bei allen Versuchen $2 \cdot 10^{-3} M$. Die zugesetzten Mengen Sc wurden so gewählt, daß mindestens 20 Moleküle Oxin auf 1 Atom Scandium vorhanden waren. Die Volumina der beiden Phasen betrugen je 50 ml. Die Eichkurve in Abb. 5 ist *geradlinig*. Das ist — gleichmässige Extraktion vorausgesetzt — schon ein Beweis für die Gültigkeit des Beer'schen Gesetzes. Zur weiteren Prüfung führten wir ausserdem folgende zwei Versuche durch: Bei Versuch A schüttelten wir eine $10^{-4} M$ Scandiumlösung mit der 20-fachen, bei Versuch B mit der 15-fachen molaren Menge an Oxin unter sonst gleichen Bedingungen aus. Von den beiden so erhaltenen Lösungen verdünnten wir aliquote Teile mit reinem Benzol und maßen jeweils die Extinktionen. In beiden Fällen (Abb. 5) liegen alle Punkte auf einer durch den Nullpunkt des Koordinatensystems gehenden Geraden. Das Beer'sche Gesetz wird also befolgt.

Literatur S. 345

Kurve A fällt ausserdem mit der Eichkurve zusammen, zum Beweis, daß der Oxinüberschuß ausreichend und in beiden Fällen $p_{\mathrm{ScOx_3}}\%$ gleich groß war. Bei Versuch B war offenbar die Extraktion nicht vollständig.

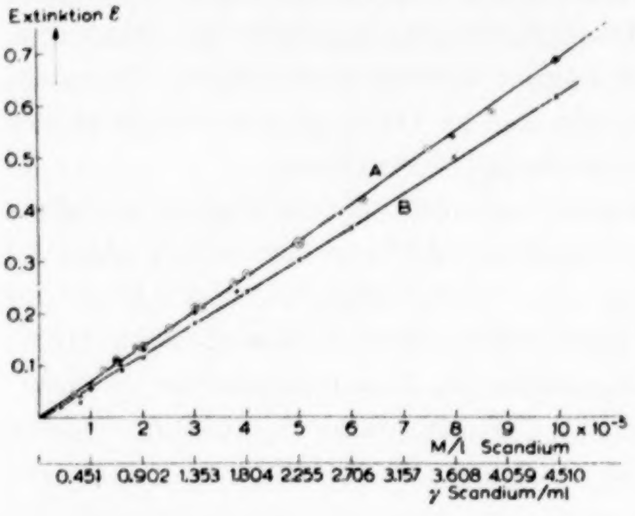

Abb. 5. Eichkurve des Scandiumoxinates und Prüfung auf Gültigkeit des Beer'schen Gesetzes. Eichkurve (⊙): Oxinkonzentration $2 \cdot 10^{-3}$ *M*ol/l; variable Sc-Mengen; Schichtdicke 1 cm. Kurve A (+): $10^{-4}M$ Sc^{+3}-Lösung mit $2 \cdot 10^{-3}M$ Oxinlösung ausgeschüttelt, mit reinem Benzol verdünnt (Oxin/Sc^{+3} = 20/1). Kurve B (×): $10^{-4}M$ Sc^{+3}-Lösung mit $1.5 \cdot 10^{-3}M$ Oxinlösung ausgeschüttelt und mit reinem Benzol verdünnt (Oxin/Sc^{+3} = 15/1).

Analysenvorschrift

Reagentien

0.1*M* salzsaure Oxinlösung (14.515 g Oxin pro Liter 0.5*N* Salzsäure).

0.5*N* Ammoniaklösung. (Die salzsaure Oxinlösung und die Ammoniaklösung, 1:10 gemischt, ergeben pH 10.2).

Benzol *p.a.*

Probe

Reine saure Scandiumlösung (Chlorid, Nitrat oder Sulfat), die u.a. als Anion kein Phosphat enthalten darf (s. Tab. II). Sc-Gehalt nicht über 180 γ (anderenfalls sind die unten angegebenen Reagentienmengen entsprechend zu erhöhen); Volumen nicht über 35 ml.

Die saure Scandiumlösung wird mit verdünnter Natronlauge auf etwa pH 6 (gegen Merck'sches Universalindikatorpapier) neutralisiert, so daß gerade noch kein Scandiumhydroxyd ausfällt. Man überführt die Lösung in einen mit Glasstopfen verschließbaren, graduierten Schüttelzylinder, gibt 1 ml der salzsauren Oxinlösung zu, schüttelt um, versetzt mit 10 ml der Ammoniaklösung und füllt mit Wasser auf 50 ml auf. Der pH-Wert dieser Lösung muss 10.2(±0.2) betragen. Dann gibt man — mit einer Pipette genau abgemessen — 50 ml Benzol zu und schüttelt sofort zwei Minuten. Man läßt die Phasen sich trennen, entnimmt dann (z.B. mit einer trockenen Pipette) einen beliebigen Teil der organischen Phase und filtriert ihn — unter Verwerfen des ersten Anteils — durch ein trockenes Filter in eine trockene Küvette. Man mißt die Extinktion mit dem Photometer ELKO II, Filter S 38 E oder einem Spectrophotometer bei 378 mμ gegen eine entsprechend hergestellte Vergleichslösung, um Fehler durch Verunreinigung der Reagentien auszuschalten. — Bei Verwendung von je 50 ml Volumen für beide Phasen beim Schütteln sind mit 1 cm-Küvetten etwa 15-250 γ, mit 5 cm-Küvetten etwa 3-60 γ Sc zu bestimmen.

Beleganalysen

In Tab. IV sind einige Beleganalysen angeführt, die nach dieser Vorschrift erhalten wurden. Die Extinktionsmessungen wurden mit dem Photometer ELKO II in 1 cm-Küvetten durchgeführt. Der mittlere Fehler der Einzelbestimmung betrug für Sc-Mengen zwischen 40-225 γ ± 2.1%. Als maximale Abweichung beobachteten wir 4%. Bei Sc-Mengen unter 40 γ stieg bei der beschriebenen Arbeitsweise der Fehler auf über 10% an. Durch Ausschütteln mit kleineren Flüssigkeitsvolumen und Verwendung von Küvetten grösserer Schichtdicke sind aber auch hier genauere Werte zu erhalten.

Wir führten ferner 15 weitere Analysen durch, bei denen der photometrischen Bestimmung von 28-170 γ Scandium eine Abtrennung von zugemischten Bestandteilen (300-4000-fache Gewichtsmenge Fe, Al, Ti, Be, Mn) nach FISCHER[2] (betr. Einzelheiten vgl. dort) unter Zusatz von je 45 - 50 mg Y_2O_3 als Spurenfänger voranging. Der mittlere Fehler der Einzelmessung betrug bei vorhergehender Trennungsoperation ± 14%, als maximale Abweichung beobachteten wir 20%. Mit Fehlern in ähnlicher Grössenordnung rechnen auch FISCHER und Mitarbeiter. Ob eventuell die Anreicherungs- und Isolierungsmethode für das Scandium mit Hilfe der Oxinatextraktion noch vereinfacht und verbessert werden kann, soll geprüft werden.

Literatur S. 345

TABELLE IV

BELEGANALYSEN FÜR DIE BESTIMMUNG VON SCANDIUM IN REINEN LÖSUNGEN

γ Sc gegeben	*γ Sc gefunden*	*γ Differenz*	*% Fehler*
14.1	15.0	+ 0.9	+ 6.4
22.5	21.0	— 2.5	— 11.1
28.1	30.3	+ 2.2	+ 7.8
33.8	38.9	+ 5.1	+ 15.1
42.2	43.9	+ 1.7	+ 4.0
45.1	45.3	+ 0.2	+ 0.4
56.3	56.6	+ 0.3	+ 0.5
67.6	69.9	+ 2.3	+ 3.4
70.5	70.0	— 0.5	— 0.7
84.6	85.2	+ 0.6	+ 0.7
90.2	91.6	+ 1.4	+ 1.6
112.6	110.7	— 1.9	— 1.7
112.6	110.2	— 2.4	— 2.1
140.7	137.7	— 3.0	— 2.1
169.0	169.0	± 0.0	± 0.0
197.1	191.1	— 6.0	— 3.0
225.0	223.2	— 1.8	— 0.8

ZUSAMMENFASSUNG

Die Verteilung des 8-Oxychinolins und des Scandiumoxinates zwischen Wasser und Benzol in Abhängigkeit vom pH-Wert der wässrigen Phase wurde untersucht. Aus der Verteilungskurve des Oxins wurden der Verteilungskoeffizient und die Dissoziationskonstanten des Oxins berechnet.

Scandiumoxinat ist im pH-Bereich 9.7-10.5 quantitativ extrahierbar, wenn mindestens 20 Moleküle Oxin pro Sc-Atom angewandt werden. Bei Gegenwart kleinerer Oxinmengen tritt eine Hydrolyse des Scandiumoxinates beim Ausschütteln ein. Eine Analysenvorschrift zur photometrischen Bestimmung kleiner Mengen Scandium wurde angegeben.

SUMMARY

The distribution of 8-hydroxyquinoline and scandium oxinate between water and benzene as a function of the pH of the aqueous phase has been studied. The distribution coefficient and the dissociation constants of the oxine are calculated from its distribution curve.

Scandium oxinate is quantitatively extractable in the pH range 9.7 - 10.5 if at least 20 molecules of oxine per 1 atom scandium are used. In the presence of smaller quantities of oxine hydrolysis of the scandium oxinate occurs on shaking. Directions are given for the photometric determination of small quantities of scandium.

RÉSUMÉ

Le partage de l'hydroxy-8 quinoléine et de l'oxinate de scandium entre l'eau et le benzène a été étudié en fonction du pH de la phase aqueuse. On a pu calculer le coefficient de partage et les constantes de dissociation de l'oxine, à partir de la courbe de partage de l'oxine.

L'oxinate de scandium peut être extrait quantitativement à un pH compris entre 9.7 et 10.5 pour un rapport d'au moins 20 molécules d'oxine pour 1 atome de scandium. En présence de plus petites quantités d'oxine, il y a hydrolyse de l'oxinate de scandium lors de l'extraction. Un dosage photométrique de petites teneurs en scandium est également décrit.

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FLUORIMETRIC DETERMINATION OF ZIRCONIUM WITH MORIN

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Alizarin sulfonic acid and quercetin[1] are probably the two reagents of greatest proved utility for the spectrophotometric determination of zirconium. The former is only moderately sensitive ($0.013\ \gamma\ \mathrm{Zr/cm^2} \equiv \log I_0/I = 0.001$ at 520 mμ) but has the advantage of reacting with few other cations in mineral acid medium. Quercetin is three times as sensitive ($0.004\ \gamma\ \mathrm{Zr/cm^2}$) as alizarin sulfonic acid but is less selective, and its use requires separation of zirconium from such elements as aluminum and titanium. In the present work morin has been studied as a fluorimetric reagent for the determination of zirconium. It is well known that morin gives a strong fluorescence with zirconium in mineral acid medium. A number of other metals fluoresce to some extent under the same conditions, so that, except for its greater sensitivity, morin is a less attractive reagent than alizarin sulfonic acid. However, by a simple expedient morin can be made to give an almost specific reaction for zirconium. It thus becomes competitive with alizarin sulfonic acid on the basis of selectivity, and its great sensitivity (about 4 times that of quercetin) makes it more valuable in trace analysis. The morin method has been examined particularly for application to the determination of zirconium in silicate rocks and materials of similar composition. Zirconium can be determined in these without any separations except those associated with the sodium carbonate decomposition of the sample.

QUANTITATIVE CHARACTERISTICS OF THE ZIRCONIUM-MORIN REACTION

The morin used in the following work was obtained from L. Light and Co., England. Although probably sufficiently pure for use as received, it was purified by crystallizing the hydrogen bromide derivative from acetic acid and converting this to morin by boiling with water. An ethyl alcohol solution of reagent was used. Standard zirconium solutions were prepared by dissolving zirconium oxychloride in dilute hydrochloric acid. Fluorescence measurements were made with a Coleman 12 B photoelectric fluorimeter (filters B_2 and PC–2).

Effect of time of standing

The fluorescence intensity of solutions containing 2.0 γ Zr and 0.20 mg of morin in 25 ml of 2.0M hydrochloric acid (4% by volume in ethyl alcohol) was measured at various times after mixing. The results in Table I show that full fluorescence intensity is attained within 5-10 minutes and that little change occurs in an hour. After two hours the intensity has decreased about 2% from the maximum.

TABLE I

EFFECT OF TIME OF STANDING ON ZIRCONIUM FLUORESCENCE INTENSITY

Time, minutes	2	5	10	15	20	30	45	60	120
Fluorescence (arbitrary units)	85	87	87	87.5	87.5	86.5	86	86	85

TABLE II

EFFECT OF ACIDITY ON FLUORESCENCE INTENSITY

(Fluorescence intensity in arbitrary units)

HCl concentration M	*Fluorescence Zr + morin*	*Fluorescence morin*	*Difference*
0.03	5	3	2
0.50	36	1	35
1.0	75	2	73
1.4	80.5	2	78.5
1.8	89	2	87
2.2	88	3	85
3.0	81	6	75
4.0	81	12	69
6.0	95	56	39

Effect of acidity

Table II gives the fluorescence intensities of mixtures containing 2.0 γ Zr, 0.20 mg of morin and 1 ml of ethyl alcohol in 25 ml of solution of varying hydrochloric acid concentration. The slight fluorescence of morin alone remains essentially constant up to about $2M$ hydrochloric acid, above which it increases. The fluorescence intensity of zirconium (blank fluorescence subtracted) reaches a maximum in approximately $1.8M$ acid. An acidity of $2M$ has been adopted as the standard acidity for the zirconium determination. A variation of $\pm$ $0.2M$ in the hydrochloric acid concentration at this acidity leads to a change of less than 2% in the fluorescence intensity of zirconium. Especially because it can be used in more strongly acid solutions, morin is superior to 3-hydroxyflavone (optimum pH 1.5 in sulfuric acid medium[2]) as a fluorimetric reagent.

Effect of morin concentration

Solutions containing 2.0 γ Zr were treated with various amounts of a 0.020% solution of morin in alcohol; the final volume was 25 ml and the acidity $2.0M$ in hydrochloric acid. The fluorescence intensity was measured after 20 minutes. From Table III it is seen that a morin concentration of 0.0008% at the specified acidity suffices. The slight decrease in the zirconium fluorescence above this concentration is very likely due to the effect of increasing alcohol concentration.

It appears that the predominant zirconium-morin species formed is the 1 Zr : 2 Mr complex, but that some 1:1 complex is also formed. The morin complexes are probably analogous to those identified in the quercetin system[1].

TABLE III

EFFECT OF MORIN CONCENTRATION ON FLUORESCENCE INTENSITY

(Fluorescence intensity in arbitrary units)

Morin concentration %	*Fluorescence Zr + morin*	*Fluorescence morin*	*Difference*
0	(1)	(1)	0
$8 \cdot 10^{-5}$	22	1	21
$1.6 \cdot 10^{-4}$	39	1	38
$2.4 \cdot 10^{-4}$	52	1.5	50.5
$3.2 \cdot 10^{-4}$	63.5	1.5	62
$4.0 \cdot 10^{-4}$	72	1.5	70.5
$6.0 \cdot 10^{-1}$	85	2	83
$8.0 \cdot 10^{-4}$	88	2.5	85.5
$1.2 \cdot 10^{-3}$	88	3	85
$1.6 \cdot 10^{-3}$	87	4	83

Effect of temperature

The fluorescence intensity of zirconium-morin solutions decreases with a rise in temperature. For example, with 2.0 γ Zr and 0.3 mg morin in 25 ml of 2.0*M* hydrochloric acid, the fluorescence intensities at 15, 25, 32, 42 and 62°C are 65.5, 56.5, 49.5, 40.5 and 26.5 (arbitrary units, blank subtracted). In the range 15-30°, a change of 1° alters the fluorescence intensity about 2%. In practice the temperature effect is eliminated by comparing the fluorescence of the sample solution with that of a standard. The temperature effect is reversible, *i.e.* a solution warmed from 15° to 32° and cooled to 15° showed the same fluorescence intensity as originally. The fluorescence of the blank decreases with temperature.

Fluorescence intensity as a function of the zirconium concentration

With 0.3 mg of morin in 25 ml of 2*M* hydrochloric acid, the fluorescence (corrected for the blank) is directly proportional to the zirconium concentration up to at least 4 γ Zr in this volume. The reproducibility of the method with the instrument used may be judged from Fig. 1. The greatest deviation from the straight line is about 3%. The lowest detectable amount of zirconium in 25 ml is about 0.025 γ, or 0.001 p.p.m., under the conditions of the present work.

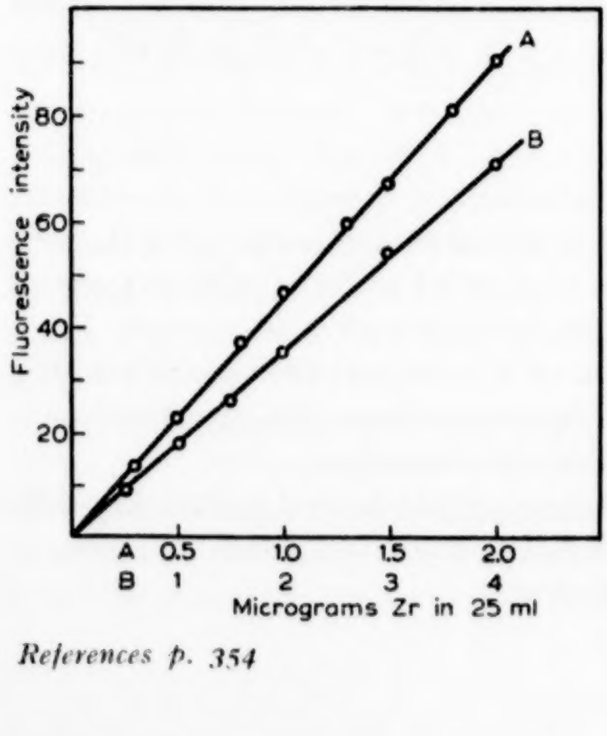

Fig. 1. Fluorescence intensity (arbitrary units) as a function of zirconium concentration. Series A contained 0.2 mg morin in 25 ml, series B 0.3 mg; solutions 2.0*M* in HCl. Instrumental sensitivity in B approximately 0.4 that in A. Fluorescence blanks (3 units for A) subtracted from all readings. Fluorescence intensity of quinine reference solution = 60 in A.

Effect of other elements

One or two mg of the following elements in 25 ml of 2*M* hydrochloric acid containing 0.3 mg of morin showed no detectable fluorescence; arsenic(V), beryllium, bismuth, cadmium, chromium(III), cobalt, copper, indium, iron(II and III), lanthanum, lithium, magnesium, manganese, mercury(II), molybdenum, nickel, tellurium(IV), thallium(I), titanium, tungsten, vanadium, zinc, yttrium and the alkaline earths. Platinum, palladium and iridium, tested in amounts of 0.2 mg, gave no fluorescence.

TABLE IV

FLUORESCENCE OF ELEMENTS WITH MORIN

(25 ml 2.0*M* hydrochloric acid, 0.3 mg morin)

Element	*Amount* *mg*	*Fluorescence*	*Fluorescence after addition of EDTA*	*Difference*
Al	1.2	21	21	0
Be	1.0	4.5	4[a]	0.5
Ga	0.15	100	100	0
Ge	1.0	38.5	37	1.5
Nb	1.8[b]	1.5	1	0.5
Sb(III)	1.0	73	73	0
Sb(V)	1.0	97	96	1
Sc	0.10	9	6	3
Sn(II)	1.0	17.5	17.5	0
Sn(IV)	1.0	18	18	0
Ta	1.6[c]	2	2	0
Th	1.0	75	75	0
U(VI)	2.0	12	12	0
Zr	0.002	70	4[a]	66

[a] This is also the fluorescence intensity of a blank
[b] Yellow-orange coloration
[c] Yellow coloration

The elements found to fluoresce in 2*M* hydrochloric acid are listed in Table IV. On the basis of the fluorescence values given, the fluorescence intensities of these elements compared to that of an equal weight of zirconium are roughly: Al 1/2000, Ga 1/50, Ge 1/1000, Th 1/400, U 1/5000, Sn 1/2000, Sb 1/500, Sc 1/500. It is evident that the direct use of morin for the determination of zirconium is of little value. The fluorescing elements must be separated or their effects must be eliminated or accounted for in a simple way. There is little likelihood of finding a complexing agent that will prevent the fluorescence of the foreign elements without affecting the zirconium fluorescence. However, the converse is possible. Ethylenediaminetetraacetic (EDTA) acid destroys the fluorescence of zirconium without affecting that of aluminum, gallium, thorium, uranium, tin and antimony. In principle this behavior should make possible the determination of zirconium in the presence of these elements when their amounts are such that their fluorescences are not much greater than the fluorescence of zirconium. Scandium will interfere in such a method because its fluorescence is partly destroyed by EDTA. Often its effect can be neglected, since in the method proposed 100 γ Sc will be equivalent to 0.1 γ Zr, and it rarely occurs in appreciable amounts. Unexpectedly, EDTA apparently diminishes the fluorescence intensity of germanium with morin. The effect is very small, 1.0 mg Ge corresponding to about 0.05 γ Zr, so that such amounts of germanium as are found in rocks will not affect the determination of zirconium.

The effect of aluminum in the EDTA-difference method was investigated in some detail because it is the fluorescent element most likely to be encountered as a major constituent of samples. It was found that the difference in fluorescence intensities before (F_1) and after (F_2) adding EDTA to destroy the zirconium fluorescence is not in general exactly equal to the fluorescence intensity of zirconium alone, and, moreover, is a function of the morin concentration. The state of affairs is represented by Fig. 2. It is seen that curve C, which represents F_1–F_2, rises above curve D, representing the fluorescence intensity of zirconium alone, and then falls below as the morin concentration is increased. The reason for this behavior is not known. It seems that aluminum has a synergistic effect on the zirconium fluorescence (or conversely) over a portion of the morin range and a reverse effect in the higher range. In part the downward trend of curve C is due to the morin liberated when zirconium is complexed with EDTA, which then increases the fluorescence intensity of aluminum, leading to a smaller value of $F_1 - F_2 = (F_{\text{Al}} + F_{\text{Zr}})_1 - (F_{\text{Al}})_2$. The fluorescence curve for aluminum, B, bends upwards as the morin concentration is increased. The same type of curve is obtained in the absence of EDTA or of EDTA and zirconium.

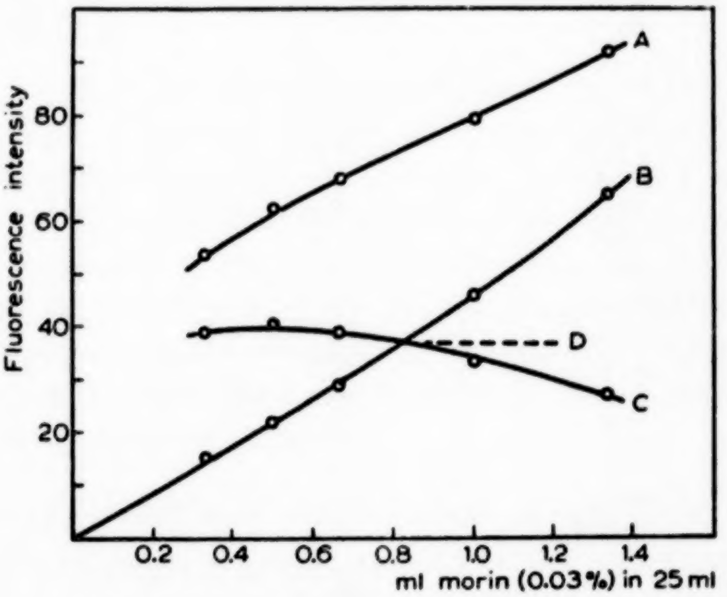

Fig. 2. Effect of aluminum (2 mg) on zirconium (1.0 γ) fluorescence as a function of morin concentration. Curve A: fluorescence of Zr + Al; curve B: fluorescence after addition of EDTA (= fluorescence of Al); curve C: B subtracted from A; D: fluorescence of Zr (1.0 γ) standard. Solutions 2.0*M* in HCl.

From the practical standpoint the important feature of the complex behavior of the system is that essentially correct results are obtained if a concentration of morin corresponding to the intersection of curves C and D is always used. A series of experiments in which the amount of zirconium was varied from 0.5 to 4 γ and that of aluminum from 0.2 to 5 mg (Al/Zr = 50 to 10,000) showed that the error in the determination of zirconium did not exceed ± 5% if a morin concentration of 0.0011% was used.

Accuracy of this order is often adequate in trace analysis.

Because of the strong color it gives with morin, ferric iron interferes in the zirconium determination. However, it is easily reduced to ferrous with mercaptoacetic (thioglycolic) acid, which is without effect. The reduction should be carried out in a solution not more acidic than 0.4*M*, else the reaction is too slow. After completion of the reduction, the hydrochloric acid concentration can be adjusted to its final value of 2.0*M*.

TABLE V

DETERMINATION OF ZIRCONIUM IN THE PRESENCE OF VARIOUS ELEMENTS BY THE EDTA DIFFERENCE METHOD

(3 mg Ca, 4 mg Mg, 4 mg Fe(III), 0.6 mg Ti, 3 mg Al; 0.1 ml 8.5% mercaptoacetic acid; final volume 25 ml)

Zr taken, γ	0.50	1.00	1.50	2.0	3.0	4.0	2.0[a]
Zr found, γ	0.51	0.99	1.47	2.0	3.1	4.0	1.85

[a] 0.5 mg Th present

Calcium, magnesium and titanium do not interfere (Table V). Phosphate and, especially, fluoride give low results, but they are automatically eliminated when the sample is decomposed by sodium carbonate fusion.

Niobium and tantalum lead to low results for zirconium when present in more than small amounts (Table VI). The principal reason for this is probably the absorption of UV radiation by their colored morinates. Niobium, whose morinate is the more strongly colored, shows the greater effect. However, up to 15 γ Nb (or Ta) can be present in 25 ml of final solution without causing appreciable error. Determination of zirconium in the standard granite G-1 according to the procedure following, after addition of 0.06% Nb (as the oxide) gave the value 0.026% ZrO_2 compared to 0.027% ZrO_2 as found by the morin method without addition. Addition of 0.05% Ta gave 0.027% ZrO_2. With 0.09% Nb and 0.32% Ta the respective ZrO_2 values found were 0.022% and 0.017%.

TABLE VI

EFFECT OF NIOBIUM AND TANTALUM ON DETERMINATION OF ZIRCONIUM

(Volume of solution 25 ml, 2*M* in hydrochloric acid, 0.3 mg morin)

Nb present, γ	80	16	1.6	—	—	—
Ta present, γ	—	—	—	80	16	1.6
Zr taken, γ	2.00	2.00	2.00	2.00	2.00	2.00
Zr found, γ	1.2	1.97	2.03	1.54	2.00	2.00

The effect of hafnium was not tested but doubtless it shows the same behavior as zirconium and will be counted with zirconium in the procedure in proportion to its fluorescence intensity with morin.

TABLE VII

DETERMINATION OF ZIRCONIUM IN GABBRO

Addition	*Zr present*[a] *p.p.m.*	*Zr found*[b] *p.p.m.*
	94	90
	98	95
	186	180
	252	250
	400	390
	520	540
50 p.p.m. each of Ge, Ta, Be, La, Th, Ga; 500 p.p.m. Cu	50	53, 47
500 p.p.m. F	50	48, 49

[a] Original Zr content of gabbro = 50 p.p.m.

[b] Double sodium carbonate fusion. The amount of zirconium recovered in the second fusion was usually small, the maximum being 20 p.p.m. with the sample containing 400 p.p.m. Zr.

DETERMINATION OF ZIRCONIUM IN SILICATE ROCKS

The sodium carbonate melt is leached with water, the washed residue is dissolved in hydrochloric acid and zirconium is determined in the solution according to the method outlined above, *i.e.*, by finding the fluorescence of the solution treated with mercaptoacetic acid and morin before and after addition of EDTA. It is usually advisable to burn the filter paper and fuse the residue with sodium carbonate to recover any zirconium not brought into solution the first time.

Samples very low in iron, *e.g.* quartz sand, should be mixed with an iron-containing material (a sub-silicic rock powder of known zirconium content serves well) before sodium carbonate fusion to prevent serious loss of zirconium when the melt is leached. U. S. Bureau of Standards glass sand No. 81 when analyzed in duplicate by the following procedure after mixing with one-fifth its weight of a gabbro gave 0.030 and 0.032% ZrO_2 (certificate value 0.031% ZrO_2), whereas if it was fused with sodium carbonate alone it gave only 0.013 and 0.014% ZrO_2.

The following procedure requires the use of a photoelectric fluorimeter. The primary filter should allow transmission of 436 mμ mercury radiation, and the secondary filter should have maximum transmission in the green ($\sim$ 525 mμ).

Special solutions

Morin, 30 mg of pure (99%) reagent in 100 ml of ethyl alcohol. The solution is stable for weeks.

Quinine, 0.75 g in 500 ml of 0.2*N* sulfuric acid. The solution is stable.

Mercaptoacetic acid solution. Dilute the strong acid (at least 85%) with nine volumes of water. Prepare fresh daily.

Zirconyl chloride. Prepare a stock solution by dissolving $ZrOCl_2.8\,H_2O$ in 4*M* hydrochloric acid to give a concentration of 10 mg Zr per milliliter. Standardize by precipitating zirconium with ammonia and igniting the precipitate to ZrO_2. Dilute the stock solution with 4*M* hydrochloric acid to obtain solutions of lower concentrations. These should be prepared shortly before use. Thus, a solution containing 10 γ Zr per ml should be used within one-half hour of preparation.

Procedure

Fuse 0.25 g of finely ground sample with 2.5 g of sodium carbonate for at least 30 minutes at high temperature. Leach the melt with about 20 ml of water on the steam bath for a few hours or allow to stand overnight at room temperature, breaking up all lumps with a stirring rod. Filter through a retentive paper and wash the residue with warm water.

References p. 354

Dissolve the residue in 15.0 ml of hot 6.0*M* hydrochloric acid and collect the solution in a 25 ml volumetric flask. Wash the paper with water and dilute filtrate and washings to 25 ml. Reserve the filter paper.

Pipet a 2.00 ml aliquot (for ∼ 100 p.p.m. Zr in the rock sample) into a 25 ml volumetric flask and add 0.2 ml of 1 : 9 mercaptoacetic acid and enough water to make the total volume approximately 18 ml. Mix and allow to stand for 5 minutes to assure complete reduction of ferric iron. Add 3.6 ml of concentrated hydrochloric acid. (If an aliquot other than 2 ml is taken, add a volume of hydrochloric acid such that the acidity will be 2.0*M* after dilution to 25 ml.) Then add 0.90 ml of morin solution and dilute to volume with water.

Set the fluorimeter at a convenient scale reading with the quinine solution and obtain the fluorescence intensities of the sample solution and (for example) a 2 γ Zr standard. The latter should have the same concentrations of hydrochloric acid, mercaptoacetic acid and morin as the sample solution. The fluorescence measurements may be made 10 minutes after the addition of morin (not later than 1 hour). Add 10 mg* of disodium ethylenediaminetetraacetate to both the sample and standard solutions and shake to dissolve. Again measure the fluorescence intensities. Find the quantity (γ) of zirconium in 25 ml of solution from the relation

$$a(F_{x_1} - F_{x_2})/(F_{s_1} - F_{s_2})$$

where a is the quantity (γ) of zirconium in the standard (25 ml) and F_{x_1} and F_{x_2} represent the first and second fluorescence intensities of the sample, and F_{s_1} and F_{s_2} those of the standard. A standard curve must be set up to establish linearity between zirconium and fluorescence intensity in the range in which the preceding expression is to be applied.

Burn the reserved paper and fuse the small amount of ash with a gram of sodium carbonate. Dissolve the melt in 5 ml of water. Without filtering, neutralize the solution with hydrochloric acid and add an excess of 8.0 ml of 6.0*M* acid, followed by 0.2 ml of 1 : 9 mercaptoacetic acid and 0.9 ml of morin solution. Dilute to 25 ml and find the fluorescence intensity before and after adding ethylenediaminetetraacetate. Multiply the amount of zirconium found by 2/25 (if a 2 ml aliquot was taken for the main determination) and add the result to the first value to obtain the total amount of zirconium.

Run a blank on the sodium carbonate. Usually a negligible amount of zirconium is found.

Notes

1. An aliquot representing 20 mg of sample will have iron, aluminum and other constituents of igneous rocks within permissible limits. If necessary, an aliquot corresponding to 40 mg can be used with most rocks. A sample of 20 mg permits the detection of about 1 p.p.m. of Zr.

2. The final 2*M* hydrochloric acid solution of zirconium should not be allowed to stand more than one-half hour before the addition of morin because of the possible hydrolysis of zirconium and consequent low results. For this reason, zirconium is determined separately in the two fusions of the sample.

3. Since scandium rarely exceeds 100 p.p.m. in rocks, its possible interference hardly needs to be considered.

SUMMARY

Zirconium can be determined fluorimetrically with morin in 2*M* hydrochloric acid in the presence of such elements as Al, Be, Ga, Sb, Sn, Th and U, which fluoresce much less strongly under the conditions, by measuring the fluorescence intensity before and after adding ethylenediaminetetraacetic acid. This substance destroys the fluorescence of zirconium only and the difference in fluorescence intensities corresponds to the concentration of zirconium in solution. The determination of zirconium in the presence of aluminum has especially been studied. Satisfactory accuracy can be obtained even when Al/Zr = 10,000, if the proper morin concentration is used. Iron does not interfere if reduced to the ferrous state with mercaptoacetic acid. Zirconium can be determined in silicate rocks without any separations except those made automatically in the sodium carbonate decomposition. Niobium and tantalum should not exceed 0.05%.

RÉSUMÉ

Le zirconium peut être dosé fluorimétriquement au moyen de la morine, dans l'acide chlorhydrique 2*M*, en présence des éléments suivants: Al, Gl, Ga, Sb, Sn, Th et U donnant une fluorescence beaucoup moins forte dans les conditions adoptées; on mesure l'intensité de fluorescence avant et après l'addition d'acide éthylènediaminotétraacétique. Ce réactif détruit la fluorescence du zirconium seulement; la différence des intensités de fluorescence correspond à la concentration du

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* This amount is suitable for 10-15 ml of solution.

zirconium en solution. Le dosage du zirconium en présence d'aluminium a été spécialement étudié. Une précision satisfaisante peut être obtenue même pour un rapport Al/Zr = 10,000, à condition de travailler avec une concentration déterminée de morine. Le fer ne gêne pas s'il est réduit en fer(II) avec l'acide mercaptoacétique. Le zirconium peut être dosé dans des silicates naturels sans séparation, à part celles effectuées normalement lors de la désagrégation au carbonate de sodium. Le niobium et le tantale ne devraient pas dépasser 0.05%.

ZUSAMMENFASSUNG

Zirkonium kann fluorimetrisch mit Morin in $2M$ Salzsäure in Gegenwart von Al, Be, Ga, Sb, Sn, Th und U, die unter den gegebenen Bedingungen viel weniger stark fluoreszieren, durch Messung der Fluoreszenz-Intensität vor und nach Zugabe von Äthylendiamintetraessigsäure bestimmt werden. Diese Substanz zerstört die Fluoreszenz von Zirkonium allein und die Differenz der Fluoreszenz-Intensitäten entspricht der Zirkoniumkonzentration in der Lösung. Die Bestimmung von Zirkonium in Gegenwart von Aluminium wurde speziell untersucht. Man kann, sogar bei einem Verhältnis von Al : Zr = 10,000, eine befriedigende Genauigkeit erreichen, wenn man die richtige Morinkonzentration verwendet. Eisen stört nicht wenn es mit Mercaptoessigsäure in den zweiwertigen Zustand übergeführt wird. Zirkonium kann in Silikatgesteinen bestimmt werden, ohne dass andere vorherige Trennungen ausgeführt werden müssen als die, welche automatisch bei dem Natriumcarbonat-Aufschluss gemacht werden. Der Gehalt an Niob und Tantal sollte 0.05% nicht überschreiten.

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SIPHONS A FLOTTEUR POUR LIQUIDES NON-CONDUCTEURS

par

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A la suite d'une étude sur la forme et les caractéristiques des siphons pour liquides conducteurs et pour liquides non-conducteurs, nous avons décrit un siphon à flotteur pour liquide non-conducteurs[1].

Dans ce dispositif, le flotteur (sphère de verre soufflé, surmontée d'un fil de platine) coulissait, par l'intermédiaire de son fil de platine, dans un manchon en laiton relié au circuit électrique; une pièce en verre en forme de couvercle, traversée en son centre par un tube de verre, maintenait le manchon métallique, donc le flotteur, dans l'axe principal du siphon.

Pour améliorer et rendre plus facile le centrage du flotteur, nous avons remplacé la pièce en verre en forme de couvercle par une couronne métallique en laiton qui vient coiffer, sans le moindre jeu, le corps du siphon. Au centre de cette couronne, est vissé un tube en argent dans lequel coulisse le flotteur (Fig. 1 A).

Le flotteur ferme le circuit électrique, et commande la rotation du plateau du collecteur de fractions, quand il arrive au contact d'une butée qui, dès ce moment, l'immobilise. Sur cette butée, la surface de contact avec le fil de platine, est en platine (Fig. 1 B).

Ce nouveau dispositif présente les avantages suivants:

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[1] J. BOVÉ, *Anal. Chim. Acta*, 11 (1954) 431.

- Facilité de réalisation (la couronne en laiton et le tube en argent sont faits au tour).
- Robustesse.
- Excellent centrage du flotteur.
- Possibilité de règler la hauteur du flotteur dans le siphon en vissant plus ou moins le tube d'argent dans la couronne en laiton.
- Dans le dispositif primitif, le flotteur coulissait dans un manchon en laiton. Après un certain temps, le laiton arrivait à s'oxyder, et le contact électrique laiton-fil de platine devenait mauvais. Avec un manchon en argent, cet inconvénient est éliminé.
- La même couronne peut être utilisée avec des siphons de différentes capacités: il suffit que le haut du corps du siphon se termine toujours par un tube de même diamètre (diamètre intérieur: 17 mm).

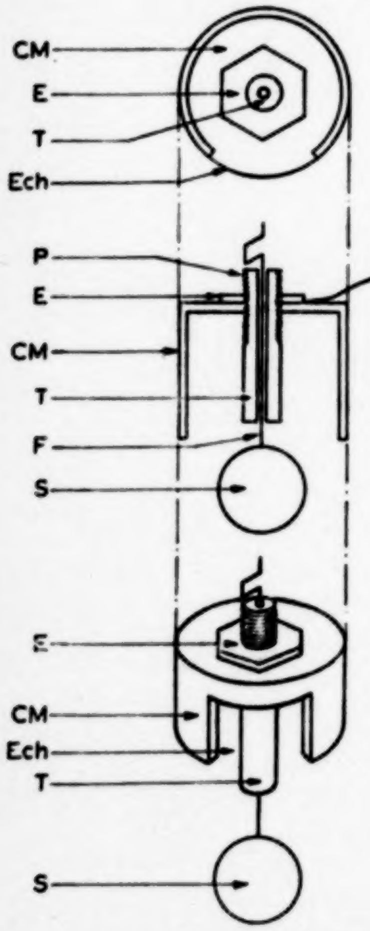

Fig. 1A. Détail du système de contact
CM : Couronne métallique
E : Écrou de serrage
Ech : Échancrure dans laquelle vient se loger le tube d'arrivée A

f : Fil électrique
F : Fil de platine du flotteur, soudé à S
P : Pas de vis
S : Sphère en verre soufflé
T : Tube en argent

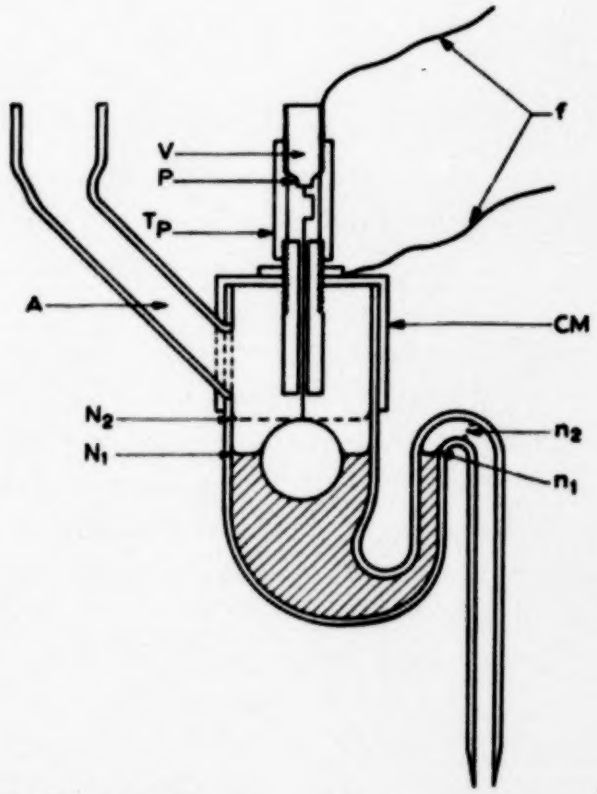

Fig. 1B. Vue d'ensemble
A : Tube d'arrivée
CM : Couronne métallique
N_1 et n_1 : Niveaux du liquide quand, au moment du contact avec P, le disque porte-tube tourne d'un cran
N_2 et n_2 : Niveaux du liquide au moment du siphonnage
P : Surface de contact platiné de la vis V
Tp : Tube transparent en matière plastique
V : Vis à surface de contact, P, platiné

La hauteur du flotteur dans le siphon est réglée de telle façon que le contact butée – fil de platine s'établisse, et ferme le circuit électrique, bien avant que le siphon ne s'amorce (Fig. 1 B). Le système de commande électronique* est conçu de sorte que le plateau du collecteur de fraction tourne d'un cran dès l'instant où le flotteur ferme le circuit électrique. Entre ce moment et celui où le siphon se vide, il s'écoule un temps plus ou moins long suivant la vitesse de remplissage du siphon, pendant lequel le circuit électrique reste fermé, mais pendant lequel le système de commande ne doit pas déclencher à nouveau le mécanisme qui fait tourner le plateau par crans.

Le courant électrique qui passe dans les contacts manchon d'argent-fil de platine et fil de platine-butée de platine doit avoir une faible intensité, de l'ordre d'une fraction de milli-ampère; avec des courants d'intensité trop élevée, il se forme des micro-arcs au moment des contacts; les surfaces de contact s'encrassent et s'opposent au passage du courant.

TABLEAU I

CARACTÉRISTIQUES DE QUELQUES SIPHONS

Volume du siphon ml	*Diamètre intérieur du corps* mm	*Diamètre intérieur du tube de sortie* mm	*Diamètre du flotteur* mm	*Diamètre du fil de platine* mm
1	12	2	8.5— 9	0.3
2	15	2	10—11	0.35
4	18	2.5	12—13	0.35
5	18	2.5	12—13	0.35

Le Tableau I donne les caractéristiques de quelques siphons. Elles ont été déterminées en faisant fonctionner divers siphons avec des solvants organiques (chloroforme, éther, benzène, éthanol, butanol normal) et non pas avec de l'eau.

Le volume du plus petit siphon à flotteur est de 1.5 ml. Le siphon de 1.5 ml ne fonctionne bien qu'avec des liquides d'assez grande densité, comme le chloroforme par exemple, mais des mélanges butanol-chloroforme jusqu'à 50% de butanol normal ou tertiaire, conviennent très bien. Il ne fonctionne pas avec le benzène. Le volume du plus petit siphon fonctionnant avec le benzène pur est 3.5 ml.

Nous avons utilisé des siphons de 1.5, 2.0 et 3.0 ml dans plus de 100 chromatographies d'acides organiques sur colonne de silice au moyen du mélange de solvants chloroforme-butanol normal ou butanol tertiaire, en recueillant lors de chaque opération plus de 400 fractions. Le nombre de ,,ratés" (deux fractions de 1.5 ,de 2.0 ou de 3.0 ml dans un même tube) était inférieur à 1 pour mille.

RÉSUMÉ

Nous rendons compte de quelques améliorations apportées dans l'exécution et dans le fonctionnement des siphons à flotteur utilisés dans le fractionnement des liquides non-conducteurs au moyen des collecteurs de fractions automatiques. Avec le nouveau dispositif décrit le nombre de ,,ratés" est inférieur à 1 pour mille.

SUMMARY

We report some improvements in the construction and functioning of the float siphon used in the fractional separation of non-conducting liquids by automatic fraction collectors. With the new device the number of failures is below one per thousand.

ZUSAMMENFASSUNG

Zur Fraktionierung nichtleitender Flüssigkeiten mit Hilfe eines Fraktionsschneiders, können Syphons mit einem Schwimmer benutzt werden. Wir berichten über einige Verbesserungen in der Ausführung und den Arbeitsbedingungen dieser Syphons. Mit dem neuen Verfahren ist die Anzahl der Versager kleiner als eins pro Tausend.

Reçu le 11 décembre 1956

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* Constructeur: M. Denis SORCINA, I.N.R.A., route de St-Cyr, Versailles.

CINÉTIQUE D'ÉLECTROLYSE DE TRACES MÉTALLIQUES AVEC DÉGAGEMENT SIMULTANÉ D'HYDROGÈNE

par

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Dans de nombreuses électrolyses réalisées dans un but analytique, on dépose quantitativement à la cathode des traces métalliques en dégageant simultanément de fortes quantités d'hydrogène. Nous nous sommes proposé de déterminer dans ces conditions l'influence de divers facteurs sur la cinétique du dépôt.

I. CONSIDÉRATIONS THÉORIQUES

Soit un cation (*i*) que nous supposerons réductible sur l'électrode envisagée et non susceptible d'être oxydé à l'anode. La concentration de (*i*) est de l'ordre de 10^{-4}-$10^{-3}M$ en solution sulfurique $1N$ par exemple.

Dans ces conditions, lorsque seul l'ion (*i*) est réduit à la cathode, on sait que le courant de migration correspondant est négligeable. Par contre, lorsque simultanément une autre espèce chimique se décharge, on observe un phénomène d'exaltation du courant de migration[1,2]. Si la densité du courant d'électrolyse est élevée (quelques ampères par cm²) par rapport à la densité limite de diffusion de l'ion considéré, ce phénomène devient prépondérant.

Nous définirons le taux d'extraction τ_i du cation (*i*) en fonction du temps par la relation:

$$\tau_i = 1 - \frac{c_{i(t)}}{c_{i(o)}}$$

$c_{i(t)}$ et $c_{i(o)}$ représentant respectivement les concentrations du cation (*i*) dans la solution à l'instant t et au temps $t = 0$

La densité du courant d'électrolyse du cation (*i*) est la somme de deux termes: un courant de migration i_M et un courant de diffusion i_D, ce dernier étant proportionnel à la concentration du cation (*i*):

$$i_D = kc_{i(t)}$$

Le courant de migration est par définition égal au produit du nombre de transport $t_{(i)}$ du cation (*i*) par la densité totale I du courant traversant la cellule:

$$i_M = t_{(i)}\, I$$

Bibliographie p. 364

En conséquence pour une cathode de surface S l'intensité $j_{(i)}$ du courant d'électrolyse de (i) est de la forme:

$$j_{(i)} = S\,(k\,c_{i(t)} + t_{(i)}\,I) \tag{1}$$

Dans les conditions posées précédemment (milieu H_2SO_4 $1N$ concentration de (i) de l'ordre de 10^{-4}-$10^{-3}M$), nous supposons que seuls existent en solution les ions H^+, HSO_4^- et (i). Le nombre de transport $t_{(i)}$ de (i) peut en conséquence s'écrire:

$$t_{(i)} = \frac{Zm_i c_{i(t)}}{m_H c_H + m_{HSO_4} c_{HSO_4} + Zm_i c_{i(t)}}$$

Les symboles m et c représentant respectivement les mobilités et les concentrations des différents ions considérés, Z désignant le nombre de charges de (i).

La concentration de (i) étant très faible vis-à-vis de celle des ions H^+ et HSO_4^-, on peut négliger au dénominateur de la relation précédente le terme $Zm_i c_{i(t)}$ d'où:

$$t_{(i)} = \frac{Zm_i c_{i(t)}}{(m_H + m_{HSO_4})c_{H_2SO_4}} \tag{2}$$

La relation (1) devient:

$$j_{(i)} = S\left[k + \frac{Zm_i I}{(m_H + m_{HSO_4})c_{H_2SO_4}}\right]\cdot c_{i(t)} \tag{3}$$

D'après la loi de Faraday:

$$j_{(i)} = -nF\,\frac{dN_{i(t)}}{dt} = -nFV\,\frac{dc_{i(t)}}{dt} \tag{4}$$

$N_{i(t)}$ représentant le nombre d'ions grammes de (i) présents en solution à l'instant t, n le nombre d'électrons mis en jeu dans la réduction cathodique de (i), V le volume de solution.

La comparaison des relations (3) et (4) donne:

$$\frac{dc_{i(t)}}{c_{i(t)}} = -\frac{S}{nFV}\left[k + \frac{Zm_i I}{(m_H + m_{HSO_4})c_{H_2SO_4}}\right]dt$$

L'intégration de cette équation permet de déterminer en fonction du temps l'expression du taux d'extraction τ_i précédemment défini:

$$\boxed{\tau_i = 1 - \frac{c_{i(t)}}{c_{i(o)}} = 1 - e^{-\lambda t}} \tag{5}$$

avec
$$\lambda = \frac{S}{nFV}\left[k + \frac{Zm_i I}{(m_H + m_{HSO_4})c_{H_2SO_4}}\right]$$

II. VÉRIFICATION EXPÉRIMENTALE

A) *Dispositif*

1. Dépôt sur mercure

La cellule représentée par la Fig. 1 déjà décrite dans des mémoires précédents[3,4] a pour capacité 200 ml environ, la surface cathodique est de l'ordre de 1 cm^2, un fil de platine enroulé en spirale constitue l'anode. Du mercure s'écoulant par un tube capillaire renouvelle constamment la surface cathodique. On recueille dans un bécher l'amalgame formé.

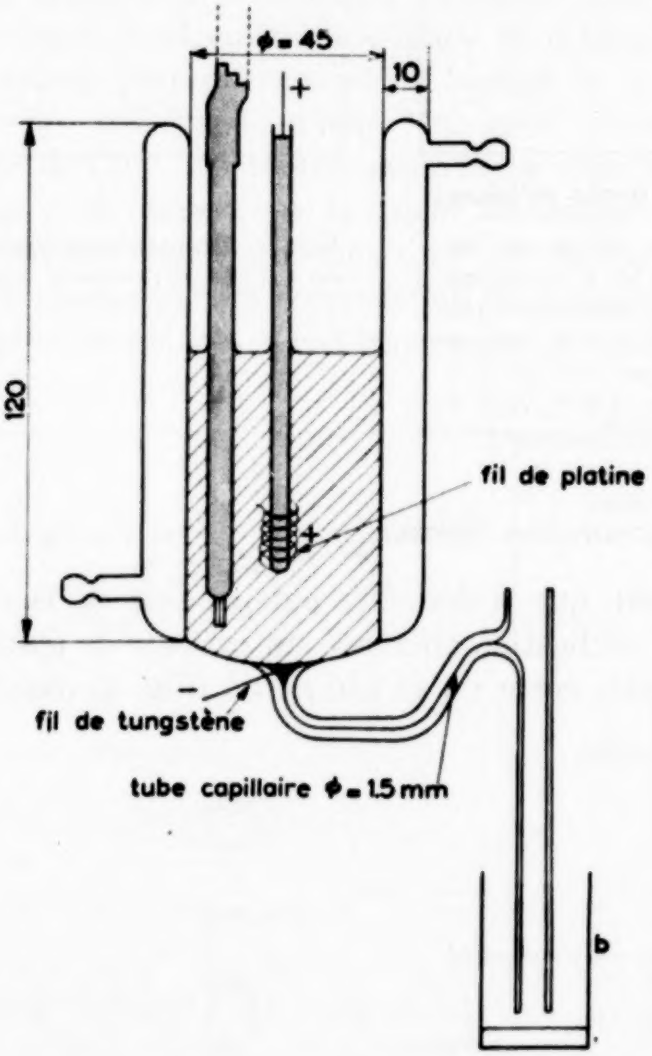

Fig. 1. Cellule à cathode de mercure renouvelée.

2. Dépôt sur platine

L'anode est identique à la précédente. Un disque de platine poli de surface 1 cm^2 est utilisé comme cathode. Le dépôt devant être réalisé uniquement sur la face en regard de l'anode, un disque en verre a été collé sur l'autre face.

B) *Résultats*

1. Nature exponentielle de la cinétique de dépôt

La courbe expérimentale $\tau = f(t)$ de la Fig. 2 représente les résultats relatifs à la décharge de Cu^{+2} sur cathode de platine. En accord avec la relation (5) la transformée logarithmique $\log (1 - \tau) = f(t)$, est bien une droite passant par l'origine (Fig. 3).

Les résultats sur cathode de mercure présentent un caractère tout à fait identique.

Bibliographie p. 364

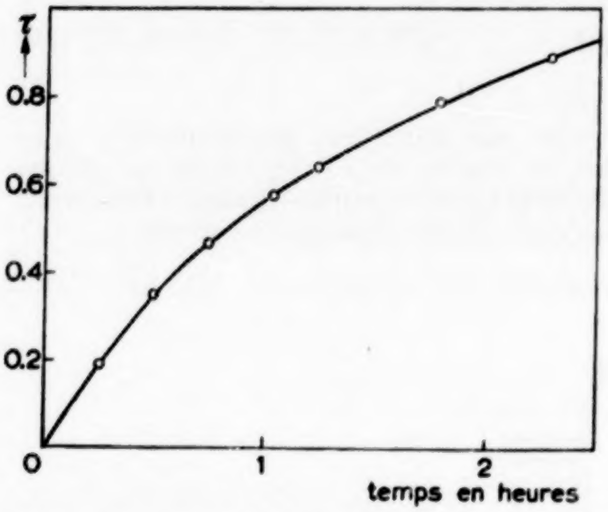

Fig. 2. Courbe de dépôt du cuivre sur cathode de platine. (H_2SO_4 1 N, V = 100 ml, surface cathodique: 1 cm², intensité totale du courant d'électrolyse: J = 2 A, température du bain électrolytique: t = 25° ± 2, concentration initiale en Cu^{+2}: $c_{i(o)}$ = 10 μg/ml, agitation par vibreur.)

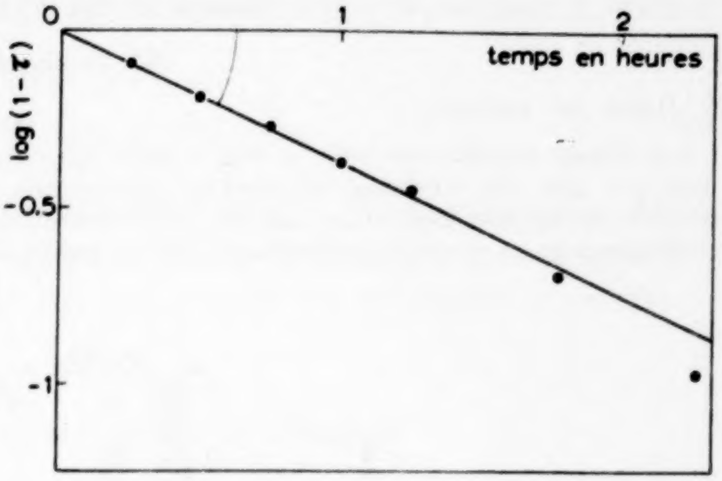

Fig. 3. Transformée logarithmique de la courbe de dépôt du cuivre sur cathode de platine.

2. *Influence de la concentration initiale*

La formule (5) établit que λ doit être indépendant de la concentration initiale $c_{i(o)}$ du cation (i). La vérification effectuée sur cathode de platine, pour des concentrations de Cu^{+2} comprise entre 1.4 et 140 μg/ml (Fig. 4) montre qu'il en est bien ainsi.

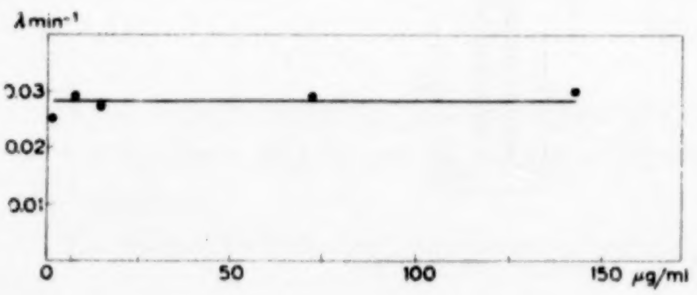

Fig. 4. Influence de la concentration initiale en cuivre. (H_2SO_4 1 N, V = 70 ml, surface de la cathode de platine: S = 2 cm², t = 20° ± 2, J = 1 A, agitation magnétique.)

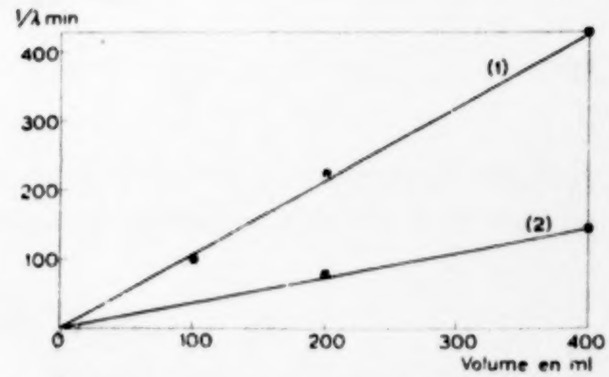

Fig. 5. Influence du volume de solution. (H_2SO_4 1 N, masse de cuivre ajoutée initialement: 1 mg, J = 1 A, t = 25° ± 1, agitation par vibreur.)
(1) Cathode de platine: S = 1 cm²,
(2) Cathode de mercure: $S \sim$ 1 cm².

3. *Influence du rapport; surface cathodique/volume de solution*

Si l'on considère la formule (5), λ doit être proportionnel à la surface cathodique S et inversement proportionnel au volume V de solution. Nous avons vérifié expérimentalement ces résultats. La Fig. 5 représente, à titre d'exemple, les variations de λ en fonction du volume V de solution obtenues sur cathode de platine et de mercure.

Bibliographie p. 364

4. Influence de l'intensité totale

D'après la relation (5), λ croît linéairement avec l'intensité totale J du courant d'électrolyse. Les courbes $\lambda = f(J)$ relatives à une cathode de mercure présentent effectivement une partie linéaire (Fig. 6).

Ordonnée à l'origine des courbes $\lambda = f(J)$

Les considérations théoriques précédentes montrent que l'ordonnée à l'origine des courbes $\lambda = f(J)$ correspond au courant limite de diffusion du cation (i). Cette dernière valeur intervient pratiquement seule lorsque la réduction du cation (i) s'effectue sans décharge simultanée d'ions H^+, aussi avons-nous déterminé la cinétique de décharge de Cu^{+2} à potentiel cathodique contrôlé. Les résultats sont représentés par la Fig. 7; on observe que la valeur numérique de λ correspondant au courant limite de diffusion relatif aux ions Cu^{+2} est de l'ordre de $5 \cdot 10^{-4}$ min^{-1}. Étant donnée l'échelle choisie pour la construction des courbes de la Fig. 7, la partie linéaire de ces dernières passe très sensiblement par l'origine.

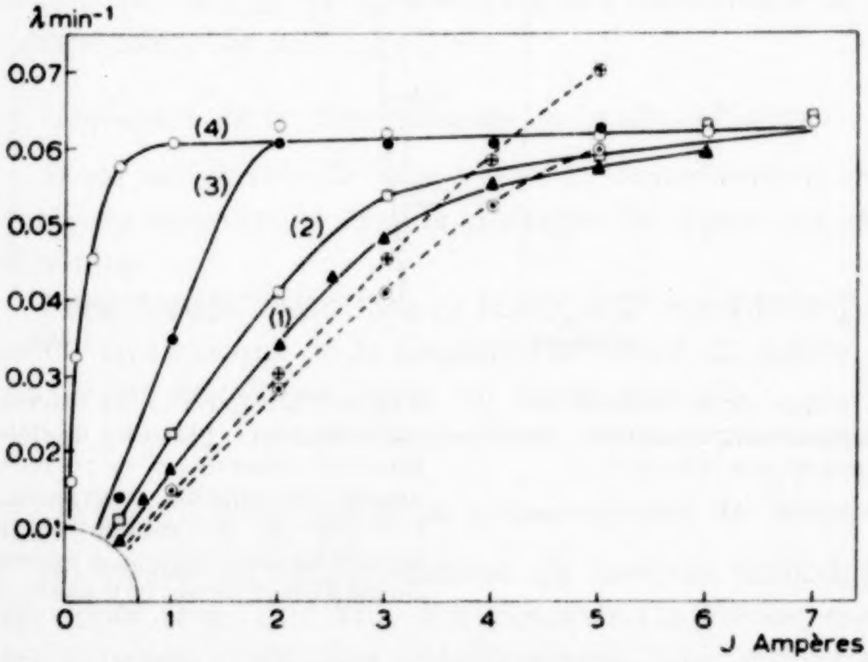

Fig. 6. Influence de l'intensité totale du courant d'électrolyse. (H_2SO_4 1 N, $V = 100$ ml, surface de la cathode de mercure: $S \sim 1$ cm^2, $t = 26° \pm 3$, concentration initiale en Cu^{+2} ou Fe^{+2}: $c_{i(o)} = 10$ μg/ml.)
Les courbes en traits pleins sont relatives à la décharge de Cu^{+2}, celles en traits discontinus à la décharge de Fe^{+2}. Courbes (1) et (1′): agitation produite uniquement par les dégagements gazeux anodique et cathodique. Courbes (2) et (3): agitation par 2 modèles d'agitateurs tournants. Courbes (4) et (4′): agitation par vibreur.

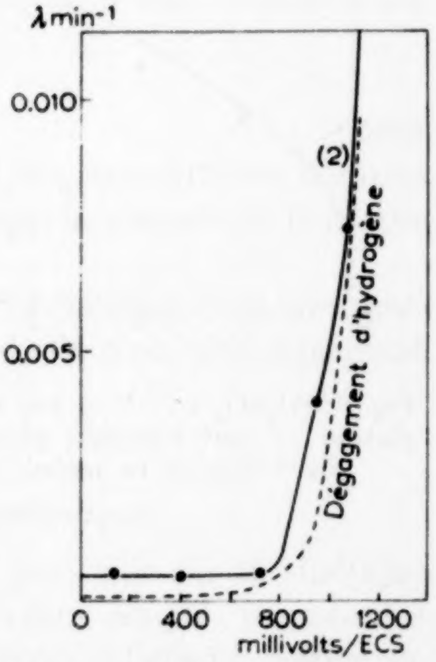

Fig. 7. Variations de la cinétique de dépôt en fonction du potentiel cathodique. (H_2SO_4 1 N, $V = 100$ ml, surface de la cathode de mercure: $S \sim 1$ cm^2, $t = 25° \pm 2$, concentration initiale en Cu^{+2}: $c_{i(o)} = 10$ μg/ml, agitation par vibreur.)

Pente de la partie linéaire des courbes $\lambda = f(J)$

Expérimentalement les pentes de la partie linéaire des courbes de la Fig. 6 sont comprises entre 10^{-2} et 10^{-1} min^{-1} A^{-1}. La relation (5) permettrait de retrouver la valeur de ces pentes à condition de connaître les mobilités relatives des ions considérés précédemment dans les conditions mêmes de l'expérience, en particulier en présence d'un dégagement tumultueux d'hydrogène.

Bibliographie p. 364

La courbe $\lambda = f(J)$ construite sur cathode de platine est également une fonction croissante de J, toutefois on n'observe pas de partie linéaire (Fig. 8).

Remarque

On utilise fréquemment pour le dosage analytique du cuivre par électrolyse une cathode de platine du type KLING-LASSIEUR, constituée par un cylindre en toile de platine. L'anode également en platine tourne à l'intérieur du cylindre et provoque l'agitation de la solution. La courbe de la Fig. 9 met également en évidence dans ce cas la croissance de la vitesse de dépôt en fonction de l'intensité totale J du courant d'électrolyse.

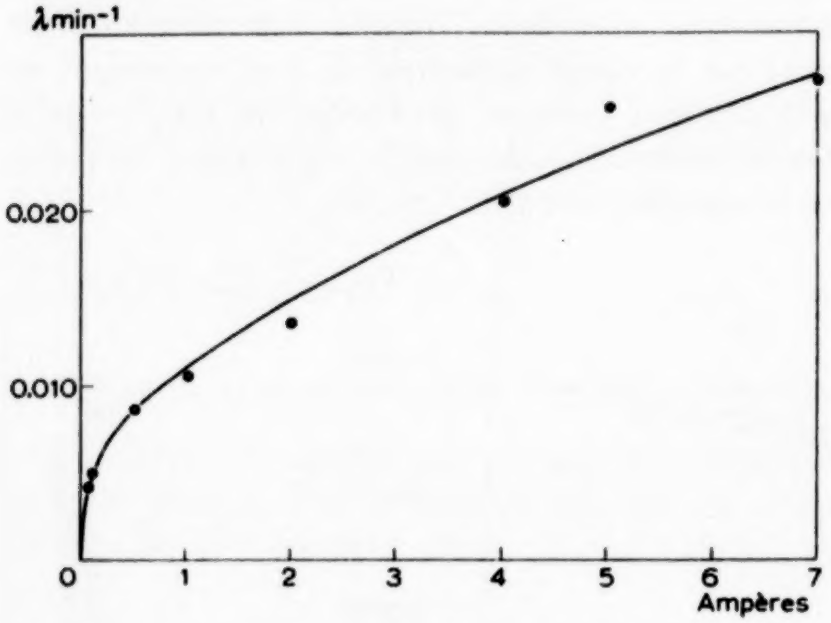

Fig. 8. (H_2SO_4 1N, $V = 100$ ml, surface de la cathode de platine: 1 cm^2, $t = 25° \pm 2$, concentration initiale en Cu^{+2}: $c_{i(o)} = 10$ μg/ml, agitation par vibreur).

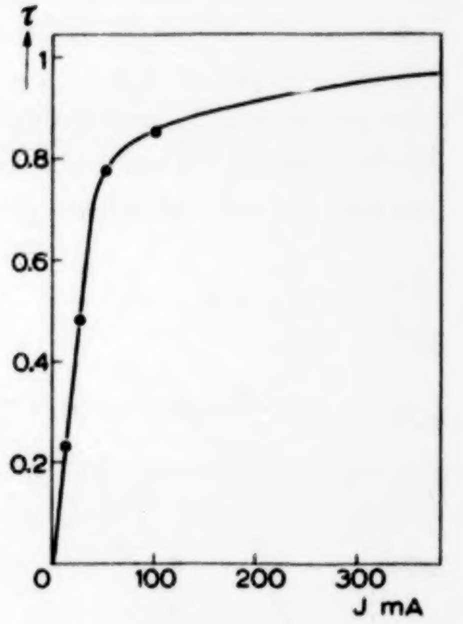

Fig. 9. (H_2SO_4 1N, $V = 110$ ml, cathode en platine modèle KLING-LASSIEUR, $S = 70$ cm^2, anode de platine tournante, $t = 25° \pm 2$, concentration initiale en Cu^{+2}: $c_{i(o)} = 9$ μg/ml, durée d'électrolyse: 10 minutes.)

5. *Influence de la température*

Une variation de la température du bain électrolytique modifie le rapport des mobilités $\dfrac{m_i}{m_H + m_{HSO_4}}$, en effet la mobilité des ions H^+ présente un coefficient de température nettement plus faible que celui des autres cations[5]. En admettant pour la mobilité des ions (i) et HSO_4^- des coefficients de température sensiblement identiques, le rapport précité doit être une fonction croissante de la température. La Fig. 10 montre effectivement que l'élévation de température du bain accélère le dépôt; toutefois, il convient de remarquer que les variations de température influent également sur la viscosité du milieu.

6. *Influence de la viscosité du milieu*

Dans le cas du dépôt de cuivre sur cathode de platine, nous avons fait varier la viscosité du milieu par addition de glycérine à la solution, les résultats sont repré-

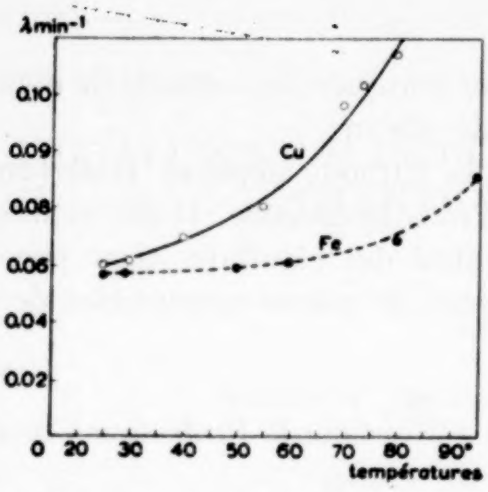

Fig. 10. Influence de la température. (H_2SO_4 1N, V = 100 ml, surface de la cathode de mercure: $S \sim 1$ cm², $J = 4$ A, concentration initiale en Cu^{+2} ou Fe^{+2}: $c_{i(o)}$ = 10 μg/ml, agitation par vibreur.)

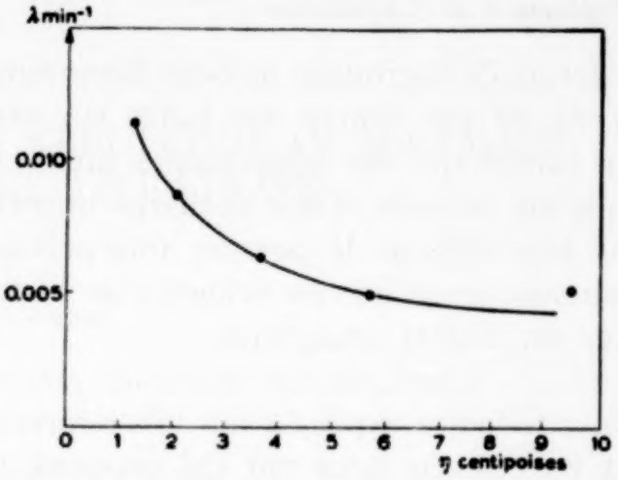

Fig. 11. Influence de la viscosité du milieu. (H_2SO_4 1N, V = 100 ml, surface de la cathode de platine: S = 1 cm², t = 31° ± 1, J = 500 mA, concentration initiale en Cu^{+2}: $c_{i(o)}$ = 10 μg/ml, agitation par vibreur.)

sentés par la Fig. 11. Les valeurs des coefficients de viscosité η sont relatifs à une température de 22°.

7. *Influence de la concentration en acide sulfurique*

Il est impossible de faire varier la concentration en H_2SO_4 sans affecter d'autres facteurs intervenant dans la cinétique du dépôt, par exemple la viscosité et la nature des ions.

Pour des concentrations en H_2SO_4 de l'ordre de 10^{-2}-$10^{-3}N$ on observe un accroissement très marqué de la cinétique de dépôt du cuivre, le dépôt n'est plus cependant un dépôt métallique, mais un dépôt d'oxyde.

La Fig. 12 traduit les résultats obtenus sur cathode de platine.

8. *Influence de la vitesse de renouvellement du mercure cathodique*

La vitesse de renouvellement du mercure cathodique peut agir sur la cinétique de dépôt (Fig. 13). Afin d'en éliminer l'influence, nous avons adopté, pour toutes les expériences décrites précédemment, une vitesse de renouvellement voisine de 6 ml/heure.

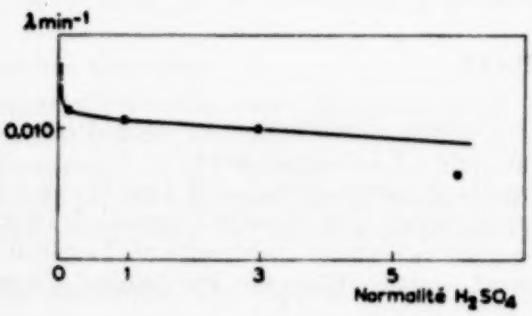

Fig. 12. Influence de la concentration en acide sulfurique. (H_2SO_4 1N, V = 100 ml, surface de la cathode de platine S = 1 cm², t = 25° ± 1, J = 1 A, concentration initiale en Cu^{+2}: $c_{i(o)}$ = 10 μg/ml, agitation par vibreur.)

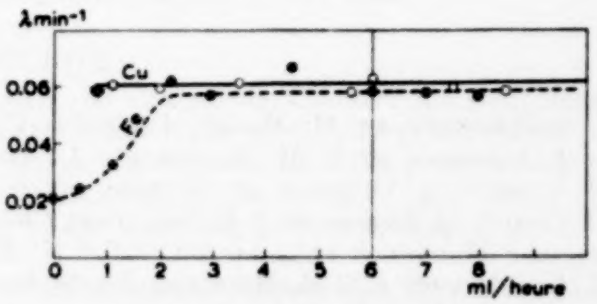

Fig. 13. Influence de la vitesse de renouvellement du mercure cathodique. (H_2SO_4 1N, V = 100 ml, surface de la cathode de mercure: $S \sim 1$ cm², t = 25° ± 2, J = 4 A, concentration initiale en Fe^{+2} ou Cu^{+2}: $c_{i(o)}$ = 10 μg/ml, agitation par vibreur.)

9. *Influence de l'agitation*

L'action de l'agitation du bain électrolytique très marquée sur cathode de mercure (Fig. 6) est par contre très faible sur cathode de platine.

La complexité des phénomènes intervenant à la cathode apparaît relativement grande en présence d'une décharge importante d'ions hydrogène. Il est manifestement très difficile de pouvoir interpréter la totalité des résultats, nous pensons, néanmoins, avoir mis en évidence un certain nombre de points susceptibles de présenter un intérêt analytique.

Nous tenons à exprimer nos vifs remerciements à Monsieur le Professeur CHARLOT dont les conseils nous ont été précieux pour cette étude.

RÉSUMÉ

Les auteurs ont déterminé à des fins analytiques l'influence d'un certain nombre de facteurs intervenant dans la cinétique de dépôt de traces métalliques sur cathode de platine ou de mercure, dans le cas de la décharge simultanée de fortes quantités d'ions hydrogène.

Les phénomènes d'exaltation du courant de migration d'un ion en présence de la décharge simultanée d'une autre espèce chimique permettent d'expliquer l'influence des différents facteurs envisagés.

SUMMARY

The authors have determined, for analytical purposes, the influence of a certain number of factors affecting the kinetics of deposition of metallic traces on a platinum or mercury cathode when there is a simultaneous discharge of a large amount of hydrogen ions.

The phenomenon of exaltation of the migration current of an ion in the presence of the simultaneous discharge of another chemical species allows an explanation of the parts played by the different factors considered.

ZUSAMMENFASSUNG

Die Verfasser ermittelten für analytische Zwecke den Einfluss einer gewissen Anzahl von Faktoren, welche in der Kinetik des Niederschlages von Metallspuren auf die Platin- bezw. Quecksilberkathode, im Falle einer gleichzeitigen Entladung grosser Mengen von Wasserstoffionen eine Rolle spielen.

Die Exaltationserscheinungen des Wanderungsstromes eines Ions in Gegenwart der gleichzeitigen Entladung einer anderen chemischen Art ermöglichen es, den Einfluss der verschiedenen in Betracht gezogenen Faktoren zu erklären.

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THE ALUMINIUM INDICATOR ELECTRODE IN ACID-BASE POTENTIOMETRIC TITRATIONS

by

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Potentiometric acid-base titrations can be performed with several types of electrodes, including metallic electrodes.

The metals investigated or used for these titrations are: chromium[1], germanium[2], tungsten[3], molybdenum[4], antimony[5], arsenic[6], copper[7], tellurium[8] and mercury[9].

In the present work the possibility of employing aluminium has been considered.

Some titrations were performed with aluminium electrodes and a characteristic behaviour was noted for this metal.

EXPERIMENTAL

The experiments consisted of potentiometric titrations, of potassium biphthalate with sodium hydroxide solutions of various concentrations, using aluminium indicator electrodes.

Materials

The electrodes were made of Merck aluminium, 99.99%, in sheets, 0.2 mm thick.

The solutions were prepared from Merck chemicals of the analytical reagent grade.

The nitrogen, supplied from a tank, was purified by passing through H_2SO_4 (1:4) and soda-lime tubes.

The titrating solutions of NaOH, approximately 0.2, 0.1 and $0.01 N$ were carbonate-free.

The solutions to be titrated were prepared by dissolving, in beakers, known amounts of potassium biphthalate with 50-100 ml of boiled distilled water.

The solution for the anodic degreasing of the electrodes had the following composition: KCN 20 g/l; NaOH 40 g/l.

For the boiling of the electrodes, a saturated solution of Na_2HPO_4 was used.

Aluminium electrodes

From an aluminium sheet strips were cut, 2 mm wide and 12 cm long. One end of a strip, cleaned with emery paper, was tied with copper wire to connect it to the potentiometer; the other end, to be immersed in the solution to be titrated, was shaped in the form of a flap, 2 mm wide and 1 cm long, separated from the remaining strip by a thin stem, 1-2 cm long.

Before being used the electrodes underwent one of the following pretreatments:

(I) The electrode was dipped for 2-3 cm in the KCN alkaline solution and then electrolysed for 5 min against a platinum cathode (a thick wire, a few centimeters long), at 4.5 V. After approximately 1 min of electrolysis, a brown film detached itself from the aluminium surface, which appeared bright and homogeneous. After being rinsed carefully with water, the electrode was immersed in boiling distilled water for 2 min. Finally, it was immersed, for 10-20 hours, in a dilute solution of potassium biphthalate.

(II) After 5 min of anodic degreasing as described above, and after rinsing with water, the electrode was immersed for a few minutes in boiling Na_2HPO_4 solution.

Immediately before use, the electrodes were rinsed with distilled water.

Sometimes the surface treated seemed to be covered by a white film; in such cases the electrodes behaved in an irregular way. Accordingly, only the electrodes that had bright and homogeneous surfaces, were used for the titrations. Each electrode was used for only one titration.

Apparatus and procedure

The solution to be titrated was placed in a 250 ml beaker, closed with a polythene stopper. Passing through holes in the stopper, were:

the aluminium electrode;
one end of a KNO_3 agar bridge, which was connected to a saturated calomel electrode;
a glass stirrer;
a right-angled glass tube with a tapered end, through which nitrogen was passed;
the end of a hooked burette.

The aluminium electrode was introduced, at the height of 7-8 cm, into the longitudinal crack of a small rubber stopper, which was placed in the corresponding hole of the polythene stopper. In this way, the electrode was held firmly during titration.

The electrode was introduced into the beaker, care being taken not to rub the surface. The flap and part of the stem were immersed in the solution. Owing to the thinness of the stem, the surface immersed was not subjected to great variations brought about by the increase of the solution volume during titration.

Rubbing of the immersed surface determined variations in potential.

The stirrer was activated by a small water motor. During the titration, the rate of stirring was kept constant, because its intensity affected the potential values.

A continual flow of nitrogen above the solution was maintained during the titration, to avoid absorption of atmospheric CO_2.

A Cambridge amplifier potentiometer was used for the measurement of potentials.

The aluminium and calomel electrodes, of which the calomel was the positive one, were connected to the potentiometer by means of simple electric wires.

Because the limit value that could be measured with the Cambridge potentiometer was 1400 mV, the following device was adopted for the potential values more negative than —1400 mV. An e.m.f. of 1 V (obtained potentiometrically from an accumulator) was applied in series with the external circuit and the polarity was inverted with respect to the e.m.f. to be measured. The potential of aluminium electrode *versus* calomel electrode, was given by the value read on the potentiometer minus the 1 V added.

The titrations were carried out in the usual way. After each addition of NaOH, a time interval was necessary in order to stabilize the potential. The electrode was considered to be in equilibrium when the potential variation was inferior to 1 mV/min.

RESULTS

Titration curves

From the very first experiments it was noted that the potential of aluminium electrodes varied with the pH much more than any other known electrode. Consequently, the acid-base titration curves (potential-volume curves) obtained with aluminium electrodes were broader in the ordinate sense.

Further investigation showed that the aluminium titration curves were similar in shape to those given by the antimony electrode, but the former were approximately 3.6 times larger in the ordinate sense, with a greater slope on the alkaline side.

In the titration of approximately 13 mg of potassium biphthalate with sodium hydroxide (about 0.01*N*), the potential of the antimony electrode varied from —250 to —590 mV, with a potential interval of 340 mV from the beginning to the end of the titration; that of aluminium, from —430 to —1680 mV, with a potential interval of 1250 mV. Ratio between the two potential intervals: 3.67 (see Fig. 1).

Successive titrations showed that the value of the potential of the aluminium electrodes at the beginning of the titrations varied markedly according to the pretreatment given, and even a little when the same pretreatment had been applied. At the end of the titrations, on the alkaline side, the value almost coincided.

References p. 369

The potential range covered in a titration increased with the sodium hydroxide concentration.

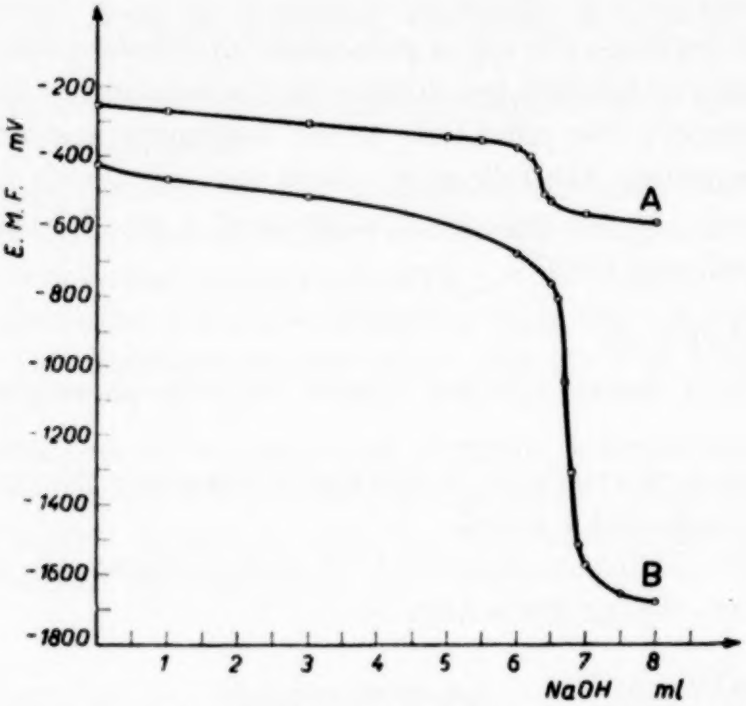

Fig. 1. Titration curves of potassium biphthalate with NaOH approx. 0.01N.
A. With antimony electrode. Biphthalate 13.1 mg
B. With aluminium electrode, subjected to pretreatment I. Biphthalate 13.9 mg

Stabilizing time

The time taken by the aluminium electrodes to reach equilibrium, after the additions of sodium hydroxide, varied from 5 to 40 min (in a few cases up to an hour). The longest stabilizing time observed was near the equivalent point. On the alkaline side, especially when the electrodes were visibly attacked by the solution, equilibrium was reached rapidly.

Influence of pretreatments

The curves obtained with the electrode subjected to pretreatment I were more similar in shape to those obtained with the antimony electrode.

With pretreatment II, the electrodes gave curves that were more sloped near the equivalent point.

The electrodes that were boiled in water, had to age in the biphthalate solution, because immediately after the boiling they assumed, in the solution to be titrated, very negative potential values and showed a very slow tendency to reach equilibrium.

Boiling in Na_2HPO_4 solution caused the electrode to reach equilibrium rapidly in the solution to be titrated, and therefore ageing was not necessary.

The potential range covered during a titration was quantitatively the same, but with pretreatment I the limits shifted to a more negative potential.

Other pretreatments did not give reproducible results.

Titrations with NaOH 0.2N

The normality of the NaOH solution, determined with phenolphthalein in air, was 0.2171N.

With aluminium electrodes, subjected to pretreatment II, the following values were obtained: 0.2204, 0.2207, 0.2203, 0.2210 and 0.2208N. Average value: 0.22064 ± 0.00023N (± 0.1%).

In all five determinations, 186 mg of potassium biphthalate were titrated, dissolved in 50 ml of solution (withdrawn per volume of the solution to be titrated). Thus, it was possible to compare the potentials at the beginning and at the end of the titrations. At the beginning, the following values were obtained: —457, —398, —364, —360 and —349 mV. At the end, after addition of 5 ml of NaOH, the values were between —1730 and —1740 mV.

Titrations with NaOH 0.1N

The average of four determinations, carried out with phenolphthalein in air, was: 0.1023N.

With the antimony electrode in a nitrogen atmosphere, the results of two determinations were: 0.1036 and 0.1037N.

With aluminium electrodes subjected to pretreatment II, the results of two determinations were: 0.1032 and 0.1031N.

Titrations with NaOH 0.01N

With the antimony electrode, the average normality for seven determinations, in nitrogen atmosphere, was: 0.009995 ± 0.00011N (± 1.1%).

With aluminium electrodes, subjected to pretreatment I, the following results were obtained: 0.01038, 0.01003, 0.01023, 0.01005, 0.01013, 0.01015, 0.01013N. Average value: 0.01015 ± 0.00008N (± 0.79%).

With aluminium electrodes, subjected to pretreatment II, the results were: 0.01025, 0.01004, 0.01004, 0.01013, 0.01014N. Average value: 0.01012 ± 0.000064N (±0.63%)

Performance of a titration

In Table I data are given concerning a titration carried out with an aluminium electrode that had been subjected to pretreatment II.

TABLE I

TITRATION OF 186 mg OF POTASSIUM BIPHTHALATE, DISSOLVED IN 50 ml OF WATER, WITH NaOH APPROX 0.2N

NaOH ml	*E —mV*	*△E mV*	*△E/△v*	*Stabilizing time min*
0	360	33	33	15
1	393	17	17	5
2	410	15	15	5
3	425	90	90	5
4	515	28	560	15
4.05	543	75	1500	15
4.10	618	891	17820	15
4.15	1509	158	3160	10
4.20	1667	20	400	5
4.25	1687	62	62	5
5.25	1749	11	11	5
6.25	1760	43	11.4	5
10	1803			5

CONCLUSIONS

1. Aluminium may be used as indicator electrode in acid-base potentiometric titrations.
2. The reproducibility and accuracy of results are dependent on special pretreatments of the surface of the electrodes.
3. The potential range covered by the aluminium electrode during a titration is much greater than that of any other known electrode; compared with the antimony electrode, its potential range is approximately 3.6 times greater.
4. The aluminium electrode reaches equilibrium with the solutions after rather a long time. Thus the titrations require more time than is necessary with other electrodes.
5. The very high variations of the aluminium electrode potential with the pH seem to denote that the experimental E-pH curve of aluminium differs from the theoretical one traced by DELAHAY, POURBAIX AND VAN RYSSELBERGHE[10] on the basis of the thermodynamic data in the literature.

ACKNOWLEDGEMENT

The author thanks Professor MARIO GIORDANI, from whom he has received guidance and encouragement in completing this work.

SUMMARY

Aluminium has been employed as an indicator electrode in potentiometric acid-base titrations. The titration curves obtained were approximately 3.6 times broader than those obtained with the antimony electrode.

RÉSUMÉ

L'auteur propose l'emploi d'une électrode d'aluminium pour les titrages alcali-acidimétriques par potentiométrie. Les courbes de titrage sont alors 3.6 fois plus étendues que celles obtenues avec l'électrode d'antimoine.

ZUSAMMENFASSUNG

Aluminium wurde als Indikator-Elektrode bei potentiometrischen Neutralisationstitrationen verwendet. Die erhaltenen Neutralisationskurven waren ungefähr 3.6 mal breiter als diejenigen, welche man mit einer normalen Antimon-Elektrode erhält.

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POTENTIOMETRIC DETERMINATION OF TETRAPHENYLBORATE WITH SILVER NITRATE

by

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INTRODUCTION

During the course of investigations in this laboratory on the identification of amines as their tetraphenylborate $B(C_6H_5)_4^-$ derivatives[1], it became necessary to determine the negative tetraphenylborate ion (TPB) content of these derivatives. A method which had reasonable speed, simplicity, and good accuracy was needed. A potentiometric titration with standard silver nitrate solution was developed for this purpose and is described in this communication.

Although no method is mentioned in the literature specifically for TPB, many procedures for determining potassium and certain nitrogen alkaloids as their insoluble TPB compounds have been described. A comprehensive bibliography on the analytical applications of sodium tetraphenylborate complete through 1955 has been compiled by BARNARD[2].

Investigators in this field have preferred the argentometric to the other methods, mainly because carbon dioxide and water do not interfere. However, all of these variations of the argentometric method utilize colored indicators, thus introducing the human error factor in the visual detection of the end-point. Moreover, their insensitivity and the extreme care required to achieve optimum conditions of the sample solution before titration, limit the utility of these methods for accurate, rapid analyses. The advantages of potentiometric titrations with silver nitrate for determining chloride ion over methods, such as those of MOHR and VOLHARD, which employ visual indicators, is well known[3]. This potentiometric technique has now been successfully extended to the determination of the negative ion content of substituted ammonium tetraphenylborates. Our method is rapid, precise and compares favorably in accuracy with the other argentometric procedures.

EXPERIMENTAL

Reagents and chemicals

The 0.6% aqueous sodium tetraphenylmetaborate solution was prepared from reagent grade solid purchased from the J.T. Baker Chemical Co. The solution was clarified with aluminum oxide according to the procedure of GLOSS[4]; stored at room temperature and filtered prior to using according to the recommendations of GLOSS and OLSON[5].

The acetone was Merck and Co. N.F. grade, which was used directly. The following chemicals — hydrochloric acid, sodium hydroxide, acetic acid, sodium acetate and silver nitrate — were all of analytical reagent grade. Distilled water was used to dissolve them.

Potassium tetraphenylborate, the primary standard for the silver nitrate solution, was precipitated at 0-5° by pouring 0.6% sodium TPB solution into a stoichiometrical equivalent of reagent grade potassium chloride in 0.3*N* hydrochloric acid solution, according to the recommendation of SPOREK AND WILLIAMS[6]. It was purified further by dissolving in acetone and reprecipitating with distilled water.

Tetra-*n*-butylammonium bromide was prepared according to the procedure of SADEK AND FUOSS[7]. The colorless crystals melted at 118-120°.

Methylpyridinium iodide, m.p. 123-125°, was synthesized and recrystallized according to BERGMANN, CRANE AND FUOSS[8].

Methyl-4-picolinium iodide, m.p. 157-158°, was prepared according to CRANE AND FUOSS[9].

Tetramethylammonium iodide, methylquinolinium iodide and 2,2'-dipyridylamine were synthesized according to CRANE[1].

The remaining organic starting materials were commercially available products. Whenever necessary, they were purified by recrystallization or simple distillation through a Vigreux column.

The organic tetraphenylborates, which were analyzed, were synthesized as follows: A small quantity (ca. 0.3 g) of either the amine, its hydrochloride or quaternary salt was dissolved in 20-30 ml of dilute hydrochloric acid. The pH of the solution was then adjusted at 2-3 by adding dilute sodium hydroxide dropwise with swirling. Then the 0.6% sodium tetraphenylborate solution was added slowly at 20-25° with stirring until only a 10-20% excess of the starting amine remained unreacted in solution. Although precipitation is immediate, the mixture was allowed to stand several minutes so as to permit growth of the crystals (usually white and dense) and insure completeness of the ionic reaction, which may be formulated as follows:

$$\mathrm{OrgN}^{+} + \mathrm{B(C_6H_5)_4}^{-} \rightarrow \mathrm{OrgNB(C_6H_5)_4} \downarrow$$

where OrgN^{+} can be an ammonium ion in any of the four possible stages of substitution. The TPB precipitates were removed by suction filtration, washed well with distilled water, and dried below 60°. Those TPborates, which showed sharp melting ranges, were pure enough for analysis. Others were recrystallized from aqueous methanol or acetone and dried over calcium chloride before they were analyzed. Some, which decomposed when warmed in these organic solvents, were recrystallized by evaporation of the solvent at room temperature.

Apparatus

Both a Thiele tube, filled with a high boiling petroleum oil and the Fisher-Johns apparatus were used to obtain melting points.

For most of the potentiometric measurements a Beckman (model H2) line-operated pH meter with a silver wire indicating electrode and a glass reference electrode (Beckman No. 1190-80) were used. A reproducible silver electrode was prepared by the method of CLARK[10]. It was cleaned between titrations by immersion in dilute sodium cyanide solution and washing with water.

Other measurements were obtained on the Sargent-Malmstadt automatic titrator[11] using a platinum indicator electrode and a shielded platinum reference electrode contained within the delivery tip.

Procedure

For each titration, approximately 0.3 meq. (60-150 mg) of the organic TPB, dried over calcium chloride, was weighed out and transferred to a 150 ml beaker. The samples were dissolved in 40 ml of acetone, and 3.0 ml each of 3*M* acetic acid and 3.0*M* aqueous sodium acetate were added to buffer the solution. Then sufficient water (34 ml) was added with stirring to make the ratio of the water to acetone in the titration medium equal 1 : 1. The inside of the beaker was coated with a thin film of vaseline just above the solution level to prevent creeping during the subsequent titration. Some of the organic borates were so insoluble in water, that only small amounts of the latter could be added before incipient precipitation from their acetone solutions occurred. In these instances just enough acetone was added to redissolve the sample completely, the ratio of acetone to water now being greater than 1 : 1. The volumes before titration were ca. 80 ml in each case. A silver indicator electrode and a glass reference electrode were immersed in the solution and connected to a Beckman pH meter, which had previously been allowed to warm up to equilibrium. Efficient magnetic stirring was started, and, after the apparatus reached a constant potential, standard aqueous silver nitrate solution was delivered slowly into the beaker from a 10 ml micro-burette, graduated every 0.02 ml. After the addition of each increment of titrant, the potential stabilized itself in a few seconds. Therefore, readings could be recorded immediately after addition except near the equivalence point, where a waiting period of one minute was sometimes required. In the vicinity of the equivalence point the silver nitrate was added in 0.01 ml increments, making possible its estimation to 0.003 ml without graphing the results. For an accurate determination of the exact equivalence point, a differential plot of the rate of change of potential with respect to volume *versus* volume of silver nitrate was employed. The maxima of these first derivative graphs are the true equivalence points. In this manner, the silver nitrate solution was standardized against potassium TPB, which had been reprecipitated from acetone with water. The volume of standard silver nitrate consumed in other titrations was then used to calculate the % of TPB in the samples.

The titration was performed more simply and rapidly by using a Sargent-Malmstadt automatic titrator in place of the Beckman pH meter. The sample to be titrated was prepared as before, except that larger amounts of buffer (5 ml each of 3*M* acetic acid and 3*M* sodium acetate) were used. The instrument was operated according to the procedure of MALMSTADT[11], using platinum electrodes. The indicator electrode makes direct contact with the solution being titrated; while the reference electrode is shielded in the delivery tip and is continually bathed by fresh titrant. The flow of silver nitrate from the 10 ml microburette stopped automatically at the equivalence point, which is found by the apparatus itself.

RESULTS AND DISCUSSION

In 1951 RAFF AND BROTZ[12] showed that sodium TPB reacted with potassium salts stoichiometrically in aqueous solutions to form a precipitate, which corresponded exactly to the formula $KB(C_6H_5)_4$. Moreover, they found that precipitation and filterability characteristics were good; the precipitate could be dried rapidly, possessing excellent thermal stability even above 120°. Thus potassium TPB was chosen to be the primary standard for the silver nitrate solution. The results of the potentiometric standardization of a silver nitrate solution using a Beckman pH meter are recorded in Table I. Seven values obtained on another silver nitrate solution (Normality = 0.06060) had a standard deviation of 0.00021 and a relative standard deviation of 0.35%.

TABLE I

STANDARDIZATION OF SILVER NITRATE WITH POTASSIUM TETRAPHENYLBORATE

KTPB mg	*$AgNO_3$ ml*	*Slope*[a]	*Normality*
177.1	8.391	31	0.05891
107.1	4.996	32	0.05983[b]
171.9	8.170	34	0.05872
119.6	5.684	45	0.05871
129.5	6.129	40	0.05896
106.6	5.052	18	0.05890
153.7	7.298	55	0.05878
194.6	9.227	32	0.05887
168.0	7.996	45	0.05864
140.3	6.656	48	0.05884

Average = 0.05881
Standard deviation = 0.00010
Relative standard deviation = 0.17%

[a] Slope at the equivalence point, expressed as $\frac{\triangle E}{\triangle V} \times 10^{-2}$, where $\triangle E$ is the potential increment in millivolts and $\triangle V$ is the volume increment in milliliters.

[b] Omitted from average.

Sodium tetraphenylborate, itself, may also be used as a primary standard, if the commercial material is recrystallized from chloroform. The relative standard deviation for six standardizations of a silver nitrate solution with this compound was found to be 0.28%. When sodium chloride was used as the primary standard, the normality value found was 5.4% lower, and the slope at the end-point was not nearly as steep.

The TPborates of hexamethylene tetramine (H) and glycine methyl ester (G) were used to determine the reproducibility and precision of the method for organic TPborates. These compounds were chosen because their Dumas nitrogen analyses agreed so well with the calculated values (see Table IV) and RUDORFF[13] had already shown that compound H was precipitated stoichiometrically from mineral acid solutions. The percentages of tetraphenylborate ion found in samples of H are shown in Table II.

TABLE II

POTENTIOMETRIC TITRATION OF HEXAMETHYLENETETRAMINE TETRAPHENYLBORATE WITH SILVER NITRATE

TPB sample[a] *mg*	*$AgNO_3$*[c] *ml*	*Slope*[b]	*$(C_6H_5)_4B^-$ %*
101.6	3.754	22	69.37
110.7	4.130	55	70.04[d]
122.4	4.538	40	69.60
162.8	5.818	75	69.13
206.0	7.376	40	69.27
235.1	8.392	40	69.05
196.0	6.978	60	68.88
125.6	4.494	58	69.21
254.3	8.986	33	68.35[d]

Average = 69.22 Theory = 69.34
Standard deviation = 0.21
Relative standard deviation = 0.30%
Relative error = −0.17%

[a] Material for the last six determinations was reprecipitated from acetone.
[b] Slopes at the equivalence points.
[c] The concentration of the solution used for the first three determinations was $0.05881\,N$, and that for the last six was $0.06062\,N$.
[d] Not included in the average.

The percentages of tetraphenylborate ion found in samples of compound G are recorded in Table III.

TABLE III

POTENTIOMETRIC TITRATION OF METHYL AMINOACETATE TETRAPHENYLBORATE WITH SILVER NITRATE

TPB sample mg	*$AgNO_3$*[a] *ml*	*Slope*	*$(C_6H_5)_4B^-$ %*
134.12	5.577	23	78.06
124.93	5.178	16	77.81
200.08	8.404	28	78.85[b]
124.86	5.161	40	77.59
126.77	5.250	31	77.75

Average = 77.80
Standard deviation = 0.17
Relative Standard deviation = 0.22%
Relative error = −0.24%

[a] Normality = 0.05881
[b] Omitted from average.

Typical data obtained in potentiometric titrations of various organic nitrogen tetraphenylborates with silver nitrate solution are listed in Table IV. The original compounds, from which the TPB derivatives were obtained, are recorded as well

TABLE IV

ANALYSIS OF TETRAPHENYLBORATE DERIVATIVES

No.	*Original compound*	*m.p., °C*[a]	*Tetraphenylborates $(C_6H_5)_4B^-$, %*		*Nitrogen, %*	
			Calcd.	*Found*	*Calcd.*	*Found*
	Quaternary compounds					
1.	Tetramethylammonium iodide	>360	81.2	84.3	3.56	3.78
2.	Tetraethanolammonium hydroxide	160-2	61.7	60.7	2.69	2.73
3.	Tetra-*n*-butylammonium bromide	229-31[b]	56.0	56.5	2.46	2.57
4.	Betaine	117-8.5	73.1	73.8	3.21	3.35
5.	Methylpyridinium iodide	240-2	77.2	76.1	3.39	3.36
6.	4-Methylpicolinium iodide	197-202	74.7	75.7	3.28	3.40
7.	Methylquinolinium iodide	196-9	68.9	69.8	2.96	3.05
	Tertiary Amines					
8.	Trimethylamine	170-2	84.1	82.6	3.70	3.69
9.	Triethylamine	172-4	75.75	76.0	3.32	3.39
10.	Triethanolamine	143-5	68.0	63.6	2.98	2.81
11.	Dimethylaniline	121-4	72.3	71.5	3.17	3.24
12.	Hexamethylenetetramine	160-1	69.34	69.2	12.16	12.09
13.	Creatinine	143-3.5	73.8	74.0	9.72	9.59
14.	Pyridine	229-31.5	79.9	[c]		
15.	Dipyridylamine	179-83	64.8	64.1	8.53	8.34
16.	Quinoline	135-7	71.04	71.3	3.12	3.16
17.	8-Hydroxyquinoline	199-202[b]	52.3[j]	55.2	4.59[j]	4.52
	Secondary Amines					
18.	Dimethylamine	157-61[d]	87.4	85.3	3.84	4.19
19.	Diethylamine	169-70	81.15	80.6	3.57	3.71
20.	Diisopropylamine	155-6	75.73	75.7	3.33	3.29
21.	Di-*n*-butylamine	144-5	71.0	67.3	3.12	3.21
22.	N-Methylaniline	105-16	74.7	[e]		
23.	Benzylmethylamine	143.5-4.0	72.3	72.8	3.18	3.15
24.	Piperidine	181.5-2.0	78.7	77.9	3.46	3.44
	Primary Amines					
25.	Methylamine	209-11	90.9	89.5	4.00	4.52
26.	Glycine methyl ester	121-3[b]	77.99	77.8	3.42	3.44
27.	Ethylamine	163-9	87.4	84.0	3.84	4.09
28.	N-Butylamine	126.5-8.5	81.3	81.6	3.57	4.14
29.	Benzylamine	178-82[b]	74.69	74.4	3.28	3.48
30.	2-Phenylethylamine	173-5	72.5	71.3	3.18	3.09
31.	Aniline	125.5-8.5	78.0	74.3[f]	3.42	4.33
32.	*p-tertiary*-amylaniline	146-9	66.0	[e]	2.90	3.05
33.	*p*-Toluidine	141-4	74.7	[c]	3.28	3.99
34.	*o*-Toluidine	118-20		[e]		
35.	*o*-Anisidine	122-4	74.7	78.8[f]	3.17	4.34
36.	2-Naphthylamine	138.5-40.5[g]	68.9	[h]	3.03	3.46
37.	*o*-Phenylenediamine[i]	139-40.5	68.7	63.7[f]	6.03	7.88

[a] Melting points are corrected values.
[b] Compound melted repeatedly at this value, indicating a true melting point.
[c] No end-point obtainable.
[d] Compound is hydroscopic.
[e] No precipitate formed upon adding silver nitrate.
[f] Slope at end-point was poor.
[g] Compound unstable in air and light.
[h] Oiled out of solution upon adding silver nitrate.
[i] Reduced silver ion to metallic silver during titration.
[j] Values are for the hypothetical addition compound, $(OXINE)_2HBC_6H_5$.

as the melting points and nitrogen contents of the resulting TPB derivatives. The latter two values indicate the degree of purity of the various derivatives analyzed. Nitrogen analyses were obtained according to the standard Dumas procedure.

As Table IV shows, it was possible to detect an end-point for all types of nitrogen compounds except the primary aromatic amines. However, it has been shown[1] that the slopes at the equivalence points were sharpest in the cases of the aliphatic and heterocyclic amine borates. The data indicate that, with the exception of compound No. 17, all of the derivatives contain only one TPB group per molecule, regardless of the number of nitrogen atoms present. Of the 31 compounds which gave detectable end-points, in 22 cases the values for TPB found were within 2% (relative) of theory; and in 12 instances the values were within 1%.

The TPB content found for compound 1 of Table IV averaged 3.1% (absolute) above the calculated (theoretical) value, and an 80% (by volume) acetone solution was needed to dissolve it prior to titration. It is interesting to note that four of the five borates derived from quaternary halide salts, namely compounds 1, 3, 6 and 7, gave high results for TPB content. This may be due to appreciable coprecipitation of the halide ion during the preparation of these derivatives, because all were prepared by adding the sodium TPB solution to an excess of the nitrogen halide salts. The bromide ion is only about one-fourth and the iodide ion one-third as heavy as the TPB group. Thus, more equivalents of silver ion would be precipitated than for the same weight of TPB, resulting in a positive error. This contamination of the borate precipitates by the original nitrogen salts would also be manifested by high results for the Dumas nitrogen determinations. The experimental values found for nitrogen contents actually were higher than the calculated for all four compounds. The exceptional halide precursor, compound 5, led to a purer borate and gave TPB analyses lower than theoretical.

The second group of borates listed in Table IV were derived from tertiary amines. One of these, compound 10, gave a very low TPB analysis; and the end-point was uncertain. Its rather high solubility in water due to the three hydroxy groups present may be a contributing factor. In another case, compound 14, no end-point at all was obtainable. This is due to the fact that since this pyridine TPborate was so insoluble in water, an 80% acetone solution was needed to dissolve it. A gravimetric determination of the silver TPB precipitate formed in this solvent yielded only 35.1% TPB. The data for compound 17 suggest that the addition of TPB ion to an acid solution of the chelating agent "OXINE" results in the precipitation of a bimolecular compound, in which the oxine tetraphenylborate is coordinated with a molecule of oxine itself.

Two of the secondary amine derivatives, compounds 18 and 22, appear to be impure. The former gave low values for TPB and a high nitrogen analysis. The hygroscopic nature of this dimethylamine derivative contributes to its four degree decomposition range. Compound 22 had an eleven degree decomposition range and yielded no precipitate with the silver nitrate solution. The compounds underwent decomposition, upon attempts to purify them by crystallization from hot aqueous methanol (2 : 3). On the other hand, the aniline borate (compound 31) was recrystallized without decomposition from hot 3 : 2 aqueous acetone; and compound 32 crystallized well from hot 1 : 5 a ueous methanol. However, these aniline derivatives, as was true of the other primary aromatic amines, either gave no precipitate with silver nitrate solution; or else the slopes at the end-points were so slight that the values obtained for TPB are uncertain. This means that these borates are not appreciably ionized in the 1 : 1 aqueous acetone titration solvent. Because the original aniline compounds are such weak bases, they apparently yield covalent precipitates instead of salts with the tetraphenylborate reagent.

FACTORS AFFECTING THE METHOD

This potentiometric method is very much like that for the determination of chloride[14], except that excess mineral acid could not be used to maintain a fixed hydrogen ion concentration around the glass reference electrode during the titration. In the preliminary experiments, we attempted to use dilute nitric acid for this purpose. However, low results were obtained, presumably because of the moderate solubility of silver TPB precipitate. This difficulty was overcome by using equivalent amounts of acetic acid and sodium acetate to buffer the titration at a pH of 5. It is possible that other buffer media might also serve the purpose.

Because only small weights of the borate derivatives were available for analysis and because detection of potentiometric end-points is easier the higher the concentration of reactants, small volumes of solution would be desirable. However, a minimum volume of 70 ml was found necessary to accomodate the working parts.

The use of as small quantities as possible of acetone to dissolve the samples, which are all quite insoluble in water, is indicated, inasmuch as silver TPB is appreciably soluble in acetone. On the other hand, small proportions of acetone in the solutions of sample limit the volume of aqueous silver nitrate, which can be delivered without causing precipitation of the unreacted organic TPB before the end-point is reached. A 1 : 1 ratio by volume of acetone to water was arbitrarily used wherever possible; and this was found to give good results. It is true that the incorporation of some acetone in the standard silver nitrate solution would somewhat obviate this danger; but the increased volatility of the resulting solvent would be a serious disadvantage.

Because silver TPB is somewhat soluble in the titration solvent, it is important that the titrant (silver nitrate solution) be standardized under conditions resembling as closely as possible those used for the organic compound being analyzed. For this reason, a tetraphenylborate (such as potassium or sodium) should be used as the primary standard instead of the halide. Since the silver halides are less soluble than the TPB precipitate in the 1 : 1 aqueous acetone solvent, use of a halide would lead to low results both for the normality of silver nitrate solution and the percentages of $(C_6H_5)_4B$ found in the organic compounds analyzed. When sodium chloride was the primary standard, the values found were 5.4% low.

When a silver electrode 2 mm in diameter was employed in conjunction with a Beckman pH meter to measure the EMF changes, considerable drifting of the potentiometer needle sometimes occurred near the equivalence point. This occasionally necessitated a considerable waiting period before the equilibrium was established, and the reading could be obtained. This difficulty can be partially alleviated by efficient stirring and removal of any precipitate, which may adhere to the silver electrode, by means of a stirring rod which remains in the solution throughout the titration. Caution must be exercised that the electrode is not rubbed too strongly,

References p. 377

or the needle will become erratic. Haphazard movement of the needle may also result, unless the glass electrode is submerged to the top (neck) of its bulb. The drifting of the needle might be reduced further by using a silver wire of smaller cross-sectional area; or by using the shielded platinum indicating electrode, which the Malmstadt titrator employs.

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SUMMARY

A simple potentiometric method for determining the tetraphenylborate ion $(C_6H_5)_4B^-$ contents of organic amine tetraphenylborate salts has been developed. The compounds are dissolved in 1 : 1 aqueous acetone; and the solution is buffered at a pH of 5 with $3M$ acetic acid and $3M$ sodium acetate. The resulting solution is then titrated with $0.06N$ aqueous silver nitrate, using a silver indicating electrode, a glass reference electrode and a Beckman pH meter to indicate EMF changes. Platinum electrodes in conjunction with the Malmstadt automatic titrator can also be used. Good end-points were obtained for all structure types except the primary aromatic amine borates. Values for $(C_6H_5)_4B^-$ found were within 2% of theory for 22 compounds so analyzed.

RÉSUMÉ

Une méthode potentiométrique simple est proposée pour le dosage de l'ion tétraphénylborique $(C_6H_5)_4B^-$ combiné sous forme de tétraphénylborate d'une amine organique. Ces composés sont dissous dans un mélange eau-acétone 1 : 1; la solution est tamponnée au pH 5 avec l'acide acétique $3M$ et l'acétate de sodium $3M$. La liqueur obtenue est ensuite titrée avec une solution aqueuse de nitrate d'argent $0.06N$ en utilisant une électrode indicatrice d'argent, une électrode de référence de verre et un pH-mètre Beckman pour enregistrer les variations de la force électromotrice. On peut également employer des électrodes de platine avec l'appareil automatique de titrage de Malmstadt. On obtient ainsi de bons résultats pour tous les types de structure, excepté les borates d'amines aromatiques primaires. Les valeurs trouvées pour $(C_6H_5)_4B^-$ ne sont jamais à plus de 2% des valeurs théoriques, pour les 22 composés étudiés.

ZUSAMMENFASSUNG

Eine einfache potentiometrische Methode zur Bestimmung des Tetraphenylborations in seinen Salzen mit organischen Aminen wird beschrieben. Man löst die Verbindungen in einem Gemisch von Aceton und Wasser (1 : 1) auf und puffert die Lösung zu pH 5 mit $3M$ Essigsäure und $3M$ Natriumacetat. In diese Lösung taucht man eine Silberindikator- und eine Glasreferenzelektrode, die beide mit einem Beckmanschen pH-Meter verbunden sind. Dann wird mit $0.06N$ Silbernitrat titriert. Platinelektroden mit dem Malmstadt'schen automatischen Titrimeter können auch verwendet werden. Die Endpunkte sind gut für alle Verbindungen mit Ausnahme der Borate der primären aromatischen Amine. Die maximale Abweichung von der Theorie bei der Analyse von 22 Verbindungen war 2%.

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POTENTIOMETRIC TITRATIONS IN NON-AQUEOUS SOLUTION

I. AN EMPIRICAL ACIDITY POTENTIAL SCALE OF TWELVE SOLVENTS

by

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INTRODUCTION

Essential for the success of any potentiometric titration is the presence of a sufficiently steep potential rise at the equivalence point in the titration curve. A rise of 200-300 mV between the half-neutralization potential (h.n.p.) of the acid (base) to be determined and the next higher plateau in the curve is sufficient for most purposes.

In order to be able to predict whether titration of a certain acid (base) or mixture of acids (bases) is feasible, and if so, to choose the most suitable solvent, one therefore has to know the relative positions of the h.n.p.'s of these acids (bases) and the limiting potentials of the available solvents.

These potentials are determined by a large number of factors. Each for one these factors are known, but their mutual correlations and their quantitative effect on the potentials mentioned are not.

In order to obtain on this subject the information required for practical applications, a number of experimental data have been collected which will be discussed in this paper.

GENERAL CONSIDERATIONS

There are four major factors having an influence on the h.n.p.'s of acids and bases in varying solvents, the principles of which are clearly understood, *viz.*,

a) The acidity and basicity of the solvent medium,
b) The "intrinsic acidity" (basicity) of the titrated acid or base,
c) The tendency of the ions involved in the titration towards formation of extraordinary stable complexes or insoluble salts,
d) The liquid junction potentials occurring at the electrode boundaries.

In addition, there is at least one factor that may exert considerable influence, but in a manner much less obvious, *viz.*,

e) The dielectric properties of the solvent medium.

Re a). The acidity and basicity of the solvent medium determine the range of potentials which can be measured, as the limits of acidity and basicity are fixed by the acidity of the solvated proton (SH_2^+) and the basicity of the solvent anion (S^-), formed by reaction of the dissolved acid (HA) or base (B) with the solvent (SH):

$$HA + SH \rightleftharpoons A^- + SH_2^+$$

$$B + SH \rightleftharpoons BH^+ + S^-$$

From a certain strength onwards all acids (bases) appear to be of the same strength, and their h.n.p.'s are determined solely by the acidity of SH_2^+ ion (basicity of S^- ion) and by the concentration of the dissolved acid. This is the so called "levelling effect" of the solvent medium (HANTSCH, *cf.* [1,2]) and in view of the large variations in acidity and basicity existing between the various solvents, it may be concluded off-hand that its influence will be a very large one.

On the other hand, the influence of the acidity of the solvent medium on the h.n.p.'s of dissolved bases, and of the basicity of the solvent medium on the h.n.p.'s of dissolved acids may be expected to be small for those bases and acids which are not "levelled". For, to a first approximation, the tendency of the solvent to accept a proton from the dissolved acid (c.q. to donate a proton to the dissolved base) will be inversely proportional to its tendency to donate it to (c.q., accept it from) the electrode. Hence, the fact that, for instance, a weak acid is more highly dissociated in a strongly basic than in a weakly basic solvent, will exert little influence on the h.n.p. of the acid. For the effect of the higher concentration of solvated protons formed in the strongly basic solvent is cancelled by their lower acidity:

$$HA + SH \rightleftarrows A^- + SH_2^+$$

$$SH_2^+ \rightleftarrows SH + H^+$$

Re b). From what has been said in the preceding paragraph, it will be clear that the "intrinsic acidity" (basicity) of the titrated acid (base) is a major factor influencing the measured h.n.p. for all acids (bases) that are not levelled. Notable exceptions occur in the cases mentioned sub *c*.

Re c). The effect of the "intrinsic acidity" (basicity) of the titrated acid (base) may be partially or completely overshadowed by the effect of the formation of extraordinary stable complexes or insoluble salts. If the salt AX formed by the titration:

$$AH + XOH \longrightarrow AX + H_2O$$

has extraordinary stability, the h.n.p. of the acid will be primarily determined by the (low) dissociation constant of this salt. If the salt is insoluble in the titration medium the h.n.p. will be largely determined by its solubility product.

Re d). If between one or both of the electrodes and the solvent medium a liquid junction potential is set up this will, of course, be included in the measured h.n.p.

Re e). The influence of the dielectric properties of the solvent medium on the dissociation of acids and the ionization of bases has been much investigated[1,2]. The effect is expected to be largest on negatively charged acids, and almost negligible on positively charged acids (protonated bases). As there exists no direct relation between the extent of acid dissociation or base ionization and the proton activity as measured by the h.n.p., the influence of the dielectric properties of the solvent medium on the h.n.p. of acidic or basic solutes is not obvious.

If the relative importance of the effects of acidity and basicity of solute and solvent medium, and of the dielectric properties of the latter are to be estimated, the formation of extraordinary stable complexes or insoluble salts has to be avoided as far as possible. This is necessary, because of the intricate dependency of the stability of complexes and the solubility of salts upon the specific chemical properties of both the titrated solute, and the titrant and the solvent medium. We have therefore endeavoured to use, and where necessary to develop, solutions of titrant acids and bases with a relatively weak tendency towards formation of stable complexes or insoluble salts in the organic solvents.

As the difficultly accessible liquid junction potentials may as a first approximation be considered constant for each solvent-electrode combination we have neither tried to determine nor to avoid them.

THE TITRANT SOLUTIONS

From the foregoing it will be clear that if comparative titrations are to be carried out in various kinds of organic solvents, the titrant solutions should meet some very specific demands. These are listed below, together with those which hold for any titrant solution.

Requirements

a) For the titrant itself

1. It should be strongly acidic (basic) in the titration medium.
2. It should not form extraordinary stable complexes or insoluble salts with the titrated solute in the titration medium.
3. It should not interfere with the functioning of the electrodes.
4. It should be stable.

b) For the solvent of the titrant

1. It should readily dissolve the titrant.
2. It should not react with the titrant.
3. It should not markedly alter the acidic, basic and dielectric properties of the titration medium.
4. It should be free from acidic and basic impurities.

As for acid titrant solutions these requirements do not present great difficulties: perchloric acid, *p*-toluene sulphonic acid and hydrochloric acid can be dissolved in most organic solvents to yield solutions meeting the above requirements in a satisfactory manner, *p*-toluene sulphonic acid has been preferred for most purposes. If these acids are used in the same solvent as is used for the titration medium the important condition sub. b.3 is completely satisfied.

Basic titrant solutions meeting the demands are much less easy to obtain. Alkali metal bases cannot be used as the tendency of the unscreened metal ions to form complexes in media of low dielectric constant is much too strong. One should therefore look for suitable ammonium type bases. The only previously described basic titrant solution which at least partially meets the above requirements, is that used by DEAL AND WYLD[3], *viz.* a solution of tetra-*n*-butylammonium hydroxide in isopropyl alcohol. This titrant solution satisfies condition b.3 only for alcoholic titration media. If the titration is carried out in an inert, or non-acidic solvent, the acidic and basic properties of the medium are gradually altered during the titration.

Much effort has therefore been spent in the present investigation in preparing solutions of tetra alkylammonium bases in inert, or at least non-acidic solvents. The choice of the solvent for the titrant is greatly limited, however, by the fact that these bases are not soluble in non-polar solvents such as benzene, while they react with many polar solvents which otherwise would be suitable, such as acetone, acetonitrile and dimethylformamide.

Pyridine appeared to be the best solvent for our purpose, although its basicity renders the titrant solutions made up with it unsuitable for the determination of h.n.p.'s of acids stronger than pyridinium ion.

Preparation and general properties of basic titrant solutions in pyridine

Solutions of tetra-*n*-butylammonium hydroxide and tri-*n*-butyl-methylammonium hydroxide in pyridine were prepared by two methods.

a) Conversion of the iodide into the hydroxide by reaction with silver oxide in aqueous medium

The aqueous suspension of the tetra-alkylammonium iodide is added to a suspension of silver oxide, (freshly precipitated with carbonate-free alkali), in water, and the mixture is stirred until the conversion is complete. The solids are filtered off, and the solvent is evaporated carefully under reduced pressure to a thick syrup. Pyridine is added, and the evaporation is continued. This procedure is repeated with successive portions of pyridine until all of the water is removed. The temperature of the solution should preferably not exceed 25°C. The solution of the hydroxide is made up to the required strength with pyridine.

All operations involved must be carried out with careful exlusion of atmospheric carbon dioxide.

b) Conversion of the iodide into the hydroxide by ion exchange in methanol

Solutions of these bases may also be prepared from the corresponding solutions in methanol by gradual displacement of the latter by pyridine. The methanolic solution of the free base is obtained by percolation of a solution of the corresponding iodide through a column of a strongly basic anion exchange resin in the OH-form (prepared with carbonate-free alkali) from which water has previously been displaced by methanol. There have been indications that Amberlite I.R.A. 400 is more stable towards strong bases than Amberlite I.R.A. 410. The fact that strongly basic ion exchange resins are generally subject to "Hofmann-degradation" should always be kept in mind, however.

Although we have several times successfully evaporated (or distilled) the methanol at temperatures higher than 25°C (bath temperatures of up to 60°C), in other cases partial decomposition of the hydroxide occurred. The slow way by evaporation below 25°C seems preferable therefore.

These bases are not stable in pyridine solution at room temperature as a consequence of "Hofmann-degradation", but they can be kept without noticeable decomposition for many months if stored in a refrigerator at —20°C when not in use.

Another inconvenience of the solutions of these bases in pyridine, which is intrinsically linked up with their extremely high basicity, is their tendency to absorb carbon dioxide. Therefore these solutions must be permanently protected from contact with the air.

THE APPROXIMATE POTENTIAL RANGES OF TWELVE SOLVENTS

The approximate potential ranges of twelve solvents considered potentially useful for titrimetry were determined from the titration curves of acids with strong bases or *vice versa*. The solvents for the titrant acids and bases were chosen carefully so as not to set a limit to the potential range of the titration medium. For example: the base limiting potential of acetonitrile can be determined by titration of any acid with Bu_3MeNOH in pyridine, as pyridine, being non-acidic, will not impose a limit on the basicity of solutions in acetonitrile. The acid limiting potential cannot be determined by titration of a strong acid in this solvent medium with the same titrant, since pyridine, by being appreciably basic, would impose its acid limiting potential on the solvent medium. It can be determined by titration of a strong acid (perchloric acid) with piperidine dissolved in acetonitrile.

Beckman 1190-75 glass electrodes and 1170 calomel electrodes were used exclusively, in conjunction with the Beckman G-modell pH-meter. To solvents of low conductivity tributylmethylammonium iodide was added ($\sim 1.5 \cdot 10^{-3}$ moles/litre) in order to obtain stable potentials. The concentration of the dissolved acids or bases was approximately $0.01N$.

Fig. 1 shows the potential ranges of twelve solvents arranged in order of increasing basicity, with titration curves schematically drawn in the diagram. It illustrates the identity of the potential ranges with the maximum heights of the titration curves to be obtained in the solvent.

This scale permits of direct comparison of the relative acidities and basicities of these solvents as manifested in titrations with the Beckman glass and calomel electrodes.

It must not be interpreted in terms of dissociation or ionization equilibria, but provides useful information on the practical possibilities of the various solvent media.

The point of 0 mV corresponds to pH = 7.80 in aqueous solution.

Passing along the scale (Fig. 1) from left to right, we meet four distinct categories of solvents:

a) The strongly acidic solvents: trifluoroacetic acid and acetic acid (1 and 2)

b) The inert solvents: chlorobenzene, acetone and acetonitrile (3, 4, 5)

c) The amphiprotic solvents: methylalcohol, isopropylalcohol and water (6, 7, 8)

d) The basic solvents: dimethylformamide, pyridine, n-butylamine and ethylenediamine (9, 10, 11, 12).

Re a). The strongly acidic solvents show very small potential ranges. It should be noted, however, that there is no certainty as to whether the acid limiting potentials in this case are really characteristic for the solvents. They might be limited by the "intrinsic" acid strength of perchlorid acid, the strongest acid used, or by failure of the glass electrode in these extremely acidic media. The latter does not seem likely, however, as a comparable potential range has been observed for acetic acid by previous investigators, using a chloranil indicator electrode[4].

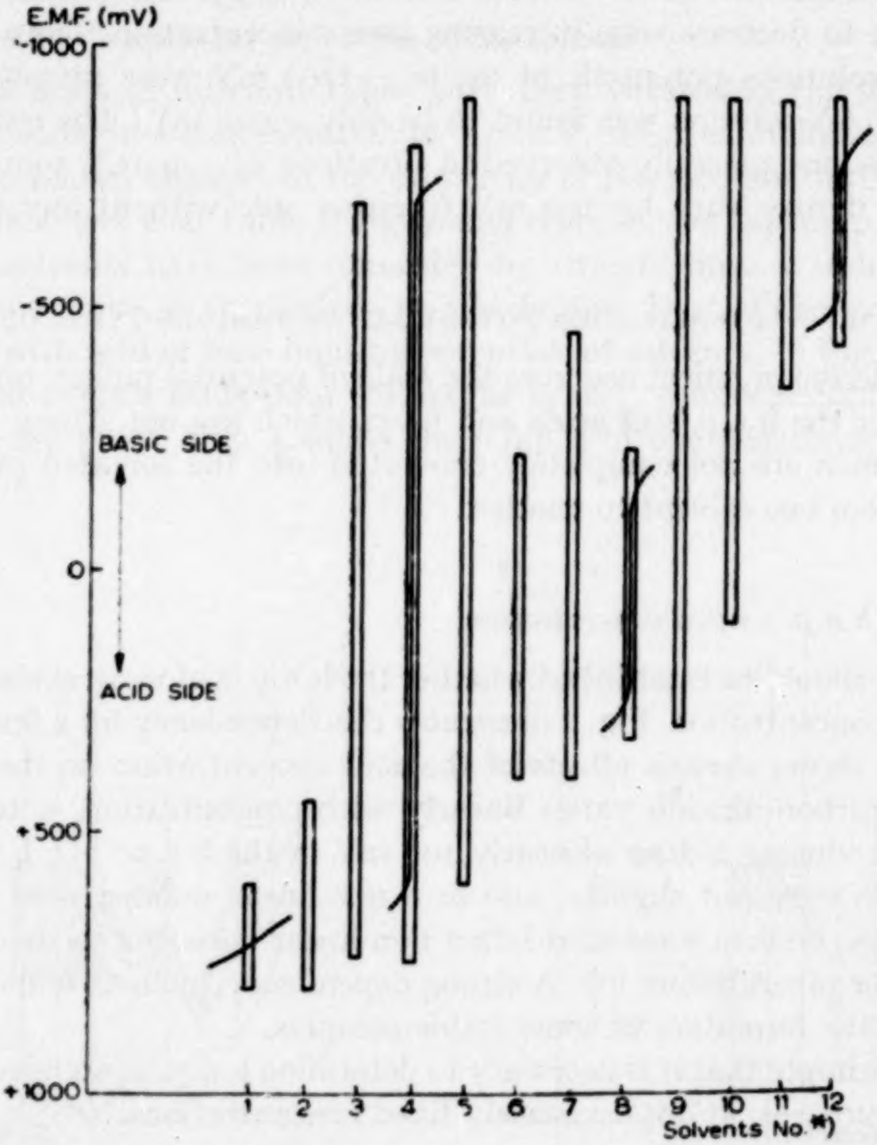

Fig. 1. Approximate potential ranges of twelve solvents arranged in the order of increasing basicity; with examples of titration curves schematically indicated

*) Solvents:

1. Trifluoroacetic acid
2. Acetic acid
3. Chlorobenzene
4. Acetone
5. Acetonitrile
6. Methylalcohol
7. Isopropylalcohol
8. Water
9. Dimethylformamide
10. Pyridine
11. *n*-Butylamine
12. Ethylenediamine

Re b). In sharp contrast to the former category, the inert solvents possess enormous potential ranges. No great value should be set on the mutual differences of base limiting potentials of these solvents shown in the scale, as these are poorly reproducible. This is probably due to the abnormal behaviour of the highly polar base molecules in media of low dielectric constant.

Re c). The amphiprotic solvents possess reproducible acid and base limiting potentials which, but for the contribution of the liquid junction potential, should reflect their inherent basicities and acidities.

Re d). The basicities of the basic solvents differ appreciably, as shown by the variation in the acid limiting potentials, which are quite reproducible. For the base limiting potentials applies what has been said sub *b*). It is certain that these potentials do not reflect the inherent acidities of the solvents. For pyridine the limiting potential has been found to decrease with increasing base concentration. Thus, in very dilute (say, 0.005*N*) solutions potentials of up to —1100 mV were measured, while the potential of a 0.6*N* solution was found to be only —200 mV! The recorded value of —900 mV is the one generally observed in titrations of —0.01*N* solutions. Even in such solutions it may vary by 100 mV to either side without any obvious cause.

THE HALF-NEUTRALIZATION POTENTIALS OF VARIOUS TYPES OF ACIDS

In order to derive practical use from the scale of potential ranges, one should know in what manner the h.n.p.'s of acids and bases which are not strong in a particular solvent (*i.e.* which are not completely converted into the solvated proton and acid anion), vary from one solvent to another.

Dependency of h.n.p.'s upon concentration

First of all it should be established whether the h.n.p.'s of weak acids are dependent upon the acid concentration. Fig. 2 illustrates this dependency for a few acids titrated in pyridine; it shows various effects of the acid concentration on the h.n.p. values. The h.n.p. of carbon-dioxide varies linearly with concentration, a tenfold increase in the latter producing a drop of nearly 100 mV in the h.n.p. The h.n.p. of benzoic acid appears to vary but slightly, and in a non-linear manner over the same concentration range, while a somewhat larger non-linear variation in the opposite direction is found for piperidinium ion. A strong dependency, such as found in the case of CO_2, indicates the formation of some stable complex.

These results imply that it is necessary to determine h.n.p.'s intended to be used for comparative purposes, at approximately fixed concentrations.

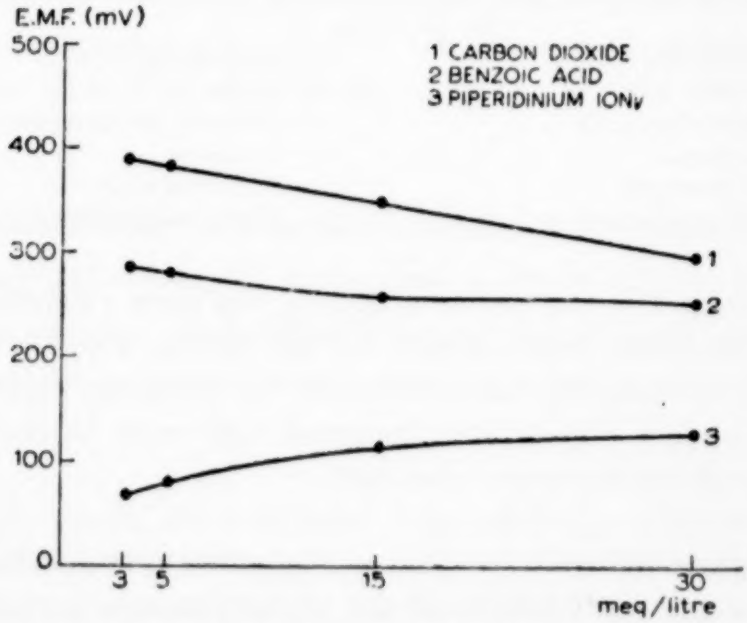

Fig. 2. Influence of the concentration of the titrated acid on its half-neutralization potential.

Variation of the concentration of added "neutral" salt tri-*n*-butylmethylammonium iodide from 0.000-0.015*N* did not exert a measurable influence on the h.n.p. of benzoic acid in pyridine.

Dependency of h.n.p.'s upon the properties of the solvent

A number of acids of different types have been titrated in the solvents of the potential range scale, in a concentration of $\sim$0.01*N*, using carefully selected titrants so as to avoid essential changes in the properties of the medium during titration.

In Figs. 3-7 incl. (see also Table I) the points representing the h.n.p.'s of the acids in the various solvents have been connected by straight lines in order to facilitate survey. These lines have, in themselves, no significance. Dashed lines connect h.n.p.'s which coincide with acid or base limiting potentials of solvents. In Fig. 3 the h.n.p.'s of six uncharged oxygen acids (four carboxylic acids^{+}, *p*-toluenesulphonic acid and sulphuric acid) are given. Fig. 4 shows the h.n.p.'s of one negatively charged acid

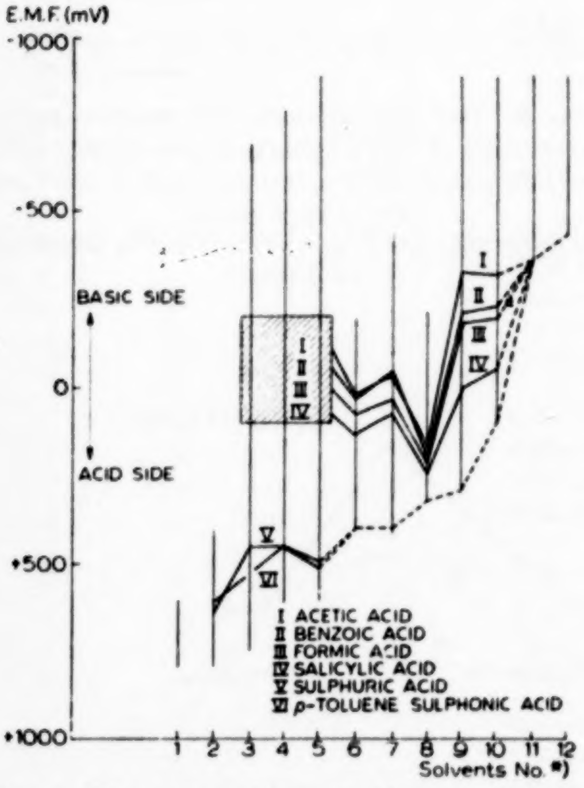

Fig. 3. The approximate half-neutralization potentials of six uncharged oxygen acids. *) Solvents: See Fig. 1. Data on the titrations in Table I.

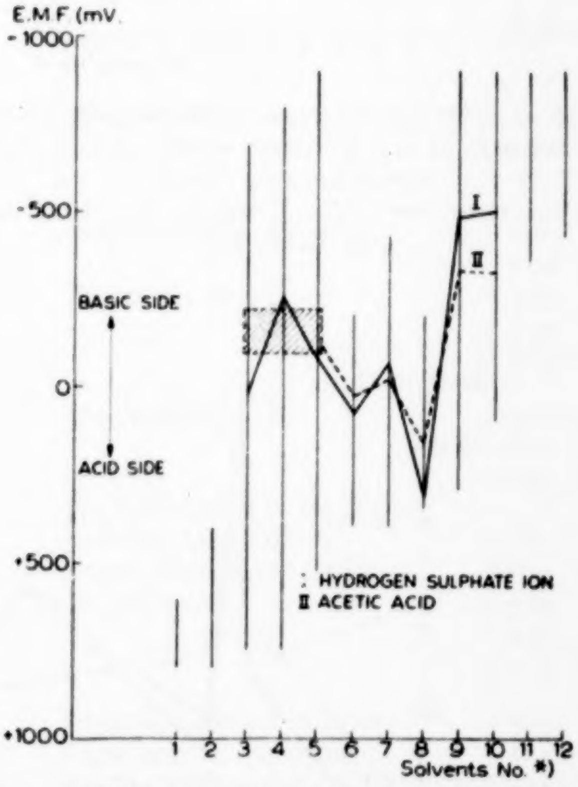

Fig. 4. The approximate half-neutralization potentials of a negative acid (as compared with those of a representative uncharged oxygen acid).
*) Solvents: See Fig. 1. Data on the titrations in Table I.

+ At the time we started this investigation we supposed that the easily available carboxylic acids and phenols would allow the study of the effects of solvent properties on the h.n.p.'s of a large range of acids over a large range of solvents.

The tendency of these acids to form polymeric hydrogen-bonded complexes (in particular with their own anions), however, rendered it impossible to obtain reproducible and significant h.n.p.'s of carboxylic acids in inert solvents, and of phenols in all but strongly basic solvents.

Hence, only carboxylic acids have been included in the present study, while the subject of hydrogen bonding effect on titrations of both classes of acids will be treated in a subsequent paper.

In Figs. 3, 4 and 6, only the approximate area in which the h.n.p.'s of carboxylic acids in inert solvents are situated could be given.

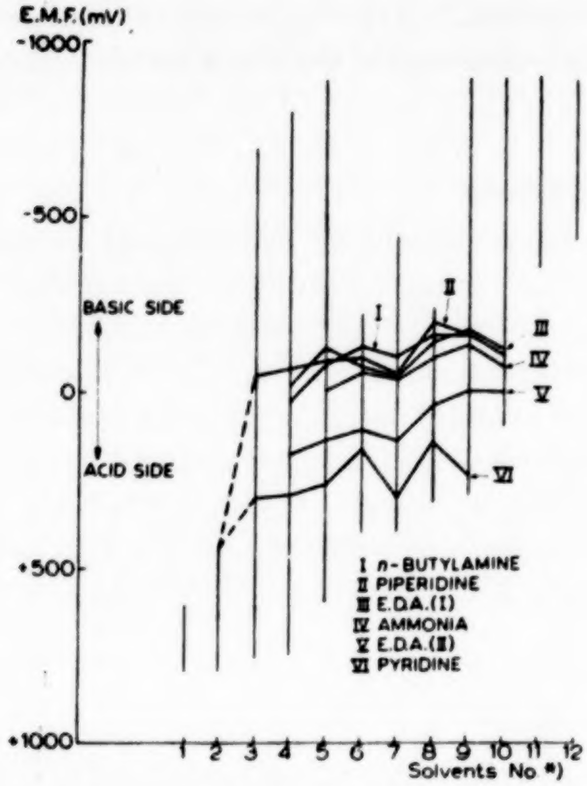

Fig. 5. The approximate half-neutralization potentials of six positive acids (denoted as corresponding bases).
*) Solvents: See Fig. 1. Data on the titrations in Table I.

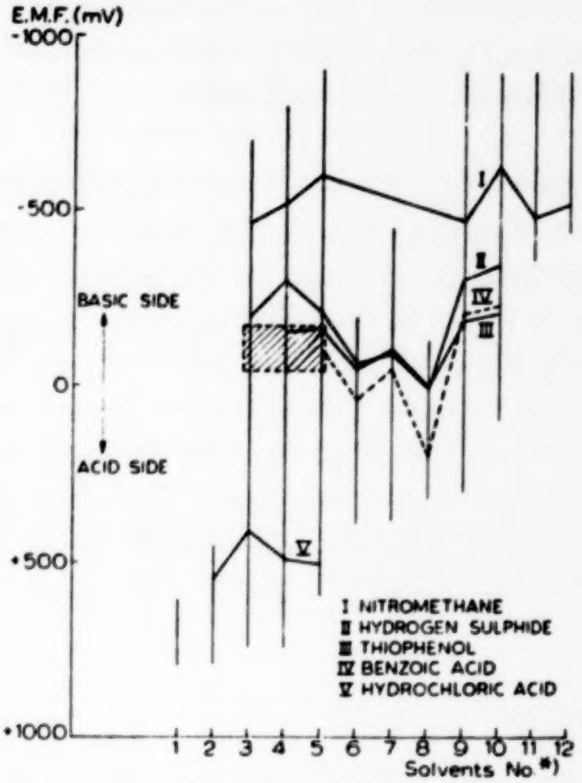

Fig. 6. The approximate half-neutralization potentials of four uncharged non-oxygen acids (as compared with a representative uncharged oxygen acid).
*) Solvents: See Fig. 1. Data on the titrations in Table I.

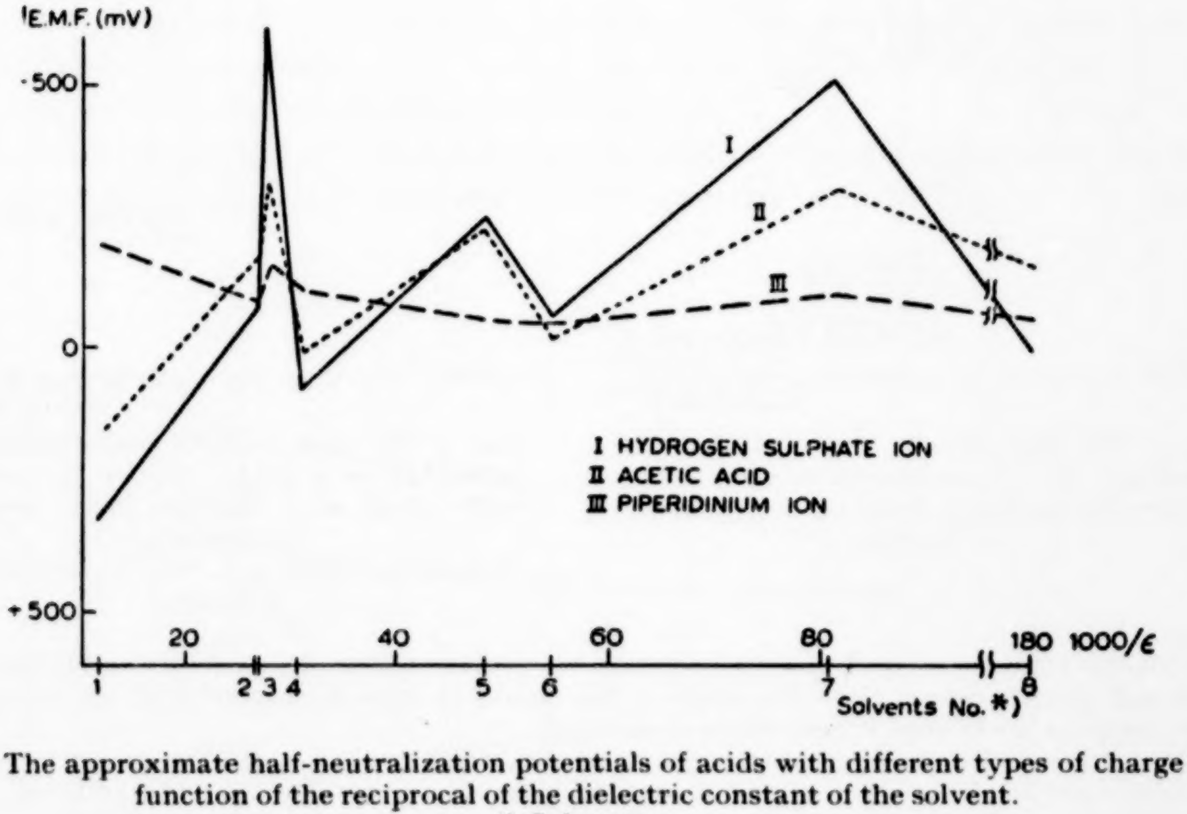

Fig. 7. The approximate half-neutralization potentials of acids with different types of charge as a function of the reciprocal of the dielectric constant of the solvent.

*) Solvents:

1. Water	5. Acetone
2. Acetonitrile	6. Isopropanol
3. Dimethylformamide	7. Pyridine
4. Methylalcohol	8. Chlorobenzene

References p. 391

TABLE I

TITRATING CONDITIONS FOR THE DETERMINATION OF APPROXIMATE h.n.p.'s PLOTTED IN Figs. 3-6*

Abbreviations

Bu$_3$MeNOH-P = Tributyl-methylammonium hydroxide in pyridine
Bu$_4$NOH-P = Tetrabutylammonium hydroxide in pyridine
Bu$_3$MeNOH-I = Tributyl-methylammonium hydroxide in I.P.A.
h.n.p. = half-neutralization potential
D.M.F. = dimethyl formamide
E.D.A. = ethylene diamine
I.P.A. = isopropyl alcohol
p.T = *p*-toluenesulphonic acid

Fig.	*Titrated solute*	*Solvent*	*Titrant (0.1N)*	*h.n.p. (mV)*
3	Acetic acid	E.D.A.	Bu$_3$MeNOH—P	—430
,,	,, ,,	*n*-Butylamine	,,	—360
,,	,, ,,	Pyridine	,,	—315
,,	,, ,,	D.M.F.	,,	—325
,,	,, ,,	Water	Bu$_3$MeNOH—I	+175
,,	,, ,,	I.P.A.	,,	—040
,,	,, ,,	Methanol	,,	+040
,,	Benzoic acid	E.D.A.	Bu$_3$MeNOH—P	—430
,,	,, ,,	*n*-Butylamine	,,	—360
,,	,, ,,	Pyridine	,,	—225
,,	,, ,,	D.M.F.	,,	—210
,,	,, ,,	Water	Bu$_3$MeNOH—I	+200
,,	,, ,,	I.P.A.	,,	—050
,,	,, ,,	Methanol	,,	+035
,,	Formic acid	Pyridine	Bu$_3$MeNOH—P	—200
,,	,, ,,	D.M.F.	,,	—190
,,	,, ,,	Water	Bu$_3$MeNOH—I	+230
,,	,, ,,	I.P.A.	,,	+030
,,	,, ,,	Methanol	,,	+080
,,	Salicylic acid	E.D.A.	Bu$_3$MeNOH—P	—430
,,	,, ,,	*n*-Butylamine	,,	—350
,,	,, ,,	Pyridine	,,	—050
,,	,, ,,	D.M.F.	Bu$_3$MeNOH—P, Bu$_4$NOH —P, Bu$_3$MeNOH—I	000
,,	,, ,,	D.M.F.	Piperidine in D.M.F.	+025
,,	,, ,,	Water	Bu$_3$MeNOH—I	+260
,,	,, ,,	I.P.A.	,,	+070
,,	,, ,,	Methanol	,,	+125
,,	Sulphuric acid I	Acetonitrile	Piperidine in acetonitrile	+505
,,	,, ,,	Acetone	Piperidine in acetone	+455
,,	,, ,,	Chlorobenzene	Bu$_3$MeNOH—I	+455
,,	,, ,,	Acetic acid	,,	+620
,,	*p*-Toluenesulphonic acid	E.D.A.	Bu$_3$MeNOH—P	—430
,,	,, ,,	*n*-Butylamine	,,	—360
,,	,, ,,	Pyridine	,,	+085
,,	,, ,,	D.M.F.	Piperidine in D.M.F.	+330
,,	,, ,,	I.P.A.	Bu$_3$MeNOH—I	+400
,,	,, ,,	Acetonitrile	Piperidine in acetonitrile	+510
,,	,, ,,	Acetone	Piperidine in acetone	+440
,,	,, ,,	Acetic acid	Pyridine in acetic acid	+605
,,	,, ,,	,, ,,	Piperidine in acetic acid	+600

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* The h.n.p.'s plotted in Figs. 3-6 have been determined under conditions that in each individual case had to be selected so as to avoid as far as reasonably feasible, *essential* changes in the medium. The majority of the values listed have been determined from several titrations.

TABLE I (continued)

Fig.	*Titrated solute*	*Solvent*	*Titrant (0.1N)*	*h.n.p.(mV)*
4	Sulphuric acid II (Hydrogen sulphate ion)	Pyridine	Bu_4NOH—P	−490
,,	,, ,, ,,	D.M.F.	Bu_3MeNOH—P	−480
,,	,, ,, ,,	Water	Bu_3MeNOH—I (0.2*N*)	+305
,,	,, ,, ,,	I.P.A.	,,	−055
,,	,, ,, ,,	Methanol	,,	+080
,,	,, ,, ,,	Acetonitrile	,,	−085
,,	,, ,, ,,	Acetone	,,	−250
,,	,, ,, ,,	Chlorobenzene	,,	+025
5	E.D.A. I	Pyridine	*p*-T in pyridine	−125
,,	,, ,,	D.M.F.	*p*-T in D.M.F.	−170
,,	,, ,,	Water	HCl in water	+035
,,	,, ,,	I.P.A.	$HClO_4$ in I.P.A.	−040
,,	,, ,,	Methanol	$HClO_4$ in methanol	−070
,,	,, ,,	Acetonitrile	$HClO_4$ in acetonitrile	−120
,,	,, ,,	Acetone	*p*-T in acetone	−015
,,	Piperidine	Pyridine	*p*-T in pyridine	−105
,,	,,	D.M.F.	$HClO_4$ in I.P.A.	−165
,,	,,	Water	,, ,, ,,	−190
,,	,,	I.P.A.	,, ,, ,,	−050
,,	,,	Methanol	,, ,, ,,	−090
,,	,,	Acetonitrile	*p*-T in acetonitrile	−085
,,	,,	Acetone	$HClO_4$ in I.P.A.	−060
,,	,,	Chlorobenzene	,, ,, ,,	−040
,,	*n*-Butylamine	Pyridine	*p*-T in pyridine	−110
,,	,,	D.M.F.	*p*-T in D.M.F.	−160
,,	,,	Water	HCl in water	−155
,,	,,	I.P.A.	$HClO_4$ in I.P.A.	−095
,,	,,	Methanol	,, ,, ,,	−125
,,	,,	Acetonitrile	*p*-T in acetonitrile	−075
,,	,,	Acetone	*p*-T in acetone	+030
,,	Ammonia (as ammoniumthiocyanate)	Pyridine	Bu_4NOH—P	−070
,,	,,	D.M.F.	Bu_3MeNOH—P	−130
,,	,,	Water	Bu_3MeNOH—I	−095
,,	,,	I.P.A.	,,	−035
,,	,,	Methanol	,,	−050
,,	,,	Acetonitrile	Bu_3MeNOH—I	+005
,,	,,	,,	Bu_3MeNOH—P	−015
,,	,,	Acetone	,,	+010
,,	E.D.A. II	Pyridine	*p*-T in pyridine	+005
,,	,,	D.M.F.	*p*-T in D.M.F.	000
,,	,,	Water	HCl in water	+035
,,	,,	I.P.A.	$HClO_4$ in I.P.A.	+140
,,	,,	Methanol	$HClO_4$ in methanol	+115
,,	,,	Acetonitrile	$HClO_4$ in acetonitrile	+140
,,	,,	Acetone	*p*-T in acetone	+180
,,	Pyridine	D.M.F.	*p*-T in D.M.F.	+240
,,	,,	Water	HCl in water	+140
,,	,,	I.P.A.	*p*-T in I.P.A.	+310
,,	,,	Methanol	*p*-T in I.P.A.	+165
,,	,,	Acetonitrile	*p*-T in acetonitrile	+270
,,	,,	Acetone	*p*-T in acetone	+300
,,	,,	Chlorobenzene	*p*-T in I.P.A.	+305
,,	,,	Acetic acid	$HClO_4$ in acetic acid	+450

TABLE I (continued)

Fig.	*Titrated solute*	*Solvent*	*Titrant (0.1N)*	*h.n.p. (mV)*
6	Nitromethane	E.D.A.	Bu_3MeNOH—P	—525
,,	,,	*n*-Butylamine	,,	—480
,,	,,	Pyridine	,,	—630
,,	,,	D.M.F.	,,	—465
,,	,,	Acetonitrile	,,	—600
,,	,,	,,	Bu_3MeNOH—I	—595
,,	,,	Acetone	Bu_3MeNOH—P	—515
,,	,,	,,	Bu_3MeNOH—I	—500
,,	,,	Chlorobenzene	Bu_3MeNOH—P	—460
,,	Hydrogen sulphide	Pyridine	,,	—345
,,	,,	D.M.F.	,,	—310
,,	,,	Water	,,	000
,,	,,	I.P.A.	,,	—100
,,	,,	Methanol	,,	—065
,,	,,	Acetonitrile	,,	—200
,,	,,	Acetone	,,	—290
,,	,,	Chlorobenzene	,,	—195
,,	Thiophenol	Pyridine	Bu_3MeNOH—P	—205
,,	,,	D.M.F.	,,	—190
,,	,,	Water	,,	—010
,,	,,	I.P.A.	Bu_3MeNOH—I	—110
,,	,,	Methanol	,,	—050
,,	,,	Acetonitrile	,,	—175
,,	,,	Acetone	,,	—160

(hydrogensulphate ion), as compared with a representative uncharged acid. Fig. 5 gives the h.n.p.'s of six positively charged acids (all ammonium-type ions).

The data presented allow of the following conclusions:

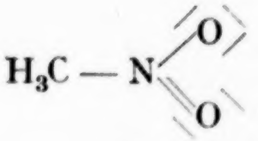
a) Increased basicity of the solvent does not lead to an increased apparent acidity of weak (*i.e.* non-levelled) acids. If there is any influence at all it works in the opposite direction.

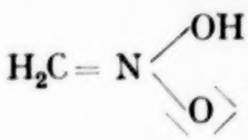
b) Increased acidity of the solvent does not distinctly enhance the apparent basicity of weak bases (in other words: does not distinctly suppress the apparent acidity of weak positive acids).

c) In the amphiprotic solvents (6,7,8) the apparent acidities of the uncharged acids and especially, of the negative acid investigated, are enormously enhanced.
It cannot be decided from our results whether this effect is due to the acidity of these solvents or to their being both moderately acidic and moderately basic. The behaviour might also be specific for solvents containing the hydroxyl group, acetic acid apparently exerting an analogous influence.

The uncharged acids considered so far are all oxygen acids. In view of the particular character of oxygen (especially of its tendency to partake in hydrogen bonding) it seems interesting to compare with the above results those of some non-oxygen acids. The h.n.p.'s of four non-oxygen acids as compared with a representative uncharged oxygen acid are shown in Fig. 6.

The h.n.p.'s of nitromethane appear to be almost equal in five solvents of widely differing basicity, while much higher (but again equal) values are obtained in two other solvents. The fact that the titrations proceed instantaneously and show no sign of association phenomena as in the case of the carboxylic acids may be considered as an indication that nitromethane actually reacts in its normal (pseudo) form A (direct abstraction of a proton from the CH_3-group) and not in the aciform B.


A
pseudo-form


B
aciform

Hydrogen sulphide and thiophenol exhibit a pattern analogous to that of the carboxylic acids (Fig. 3), though with less variation between the h.n.p.'s in different solvents.

The possible influence of the dielectric properties of the solvent medium have so far not been considered in the discussion. Fig. 7 shows the h.n.p.'s of a positive, an uncharged and a negative acid plotted against the reciprocal of the dielectric constant of the solvent. We must note here that in this graph the potentials plotted for acetic acid in acetonitrile, acetone and chlorobenzene are rather uncertain.

It appears that there is no clearly discernible influence of the dielectric constant on the h.n.p.'s of either of the three types of acids as a result of the variations caused by other factors. The graph clearly illustrates once more the constancy of the h.n.p.'s of positive acids through all changes of solvent medium.

SURVEY AND CONCLUSIONS

a) The supposition has been advanced that the feasibility of potentiometric titration of acids (bases) in non-aqueous solvents is primarily dependent upon the "intrinsic" acidity of the acid (basicity of the base) and upon the potential range of the solvent medium, unless extraordinary stable complexes or insoluble salts are formed as products of the titration.

b) For the purpose of checking this supposition, titrant solutions have been selected (and, in part, developed*) that were expected to possess a low tendency towards formation of extraordinary stable complexes or insoluble salts with the acids to be titrated in organic solvents.

c) With the aid of these titrant solutions empirical potential ranges of twelve solvents have been determined, and with the data obtained a practical potential range scale has been drawn.

d) A number of acids of various types have been titrated in these solvents and their h.n.p.'s have been plotted in the potential range scale.

e) The results are in agreement with the supposition mentioned sub a), except as regards the negative acid investigated, and as regards the neutral acids in amphiprotic solvents. If the variations in the h.n.p.'s of individual acids and bases in different solvents are considered relative to the variations in acid and base limiting potentials of the solvents, we may state more specifically that:

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* The titrants developed by the present authors consist of tetra-alkylammonium bases dissolved in pure pyridine.

1. The h.n.p.'s of bases (c.q. positive acids) are constant over the whole range of solvents in which they are not levelled.
2. The h.n.p.'s of uncharged acids are constant over the whole range of non-amphiprotic solvents in which they are not levelled.
3. The h.n.p.'s of uncharged and negative acids in amphiprotic solvents are largely shifted to the positive (acidic) side compared with those in other solvents. This effect is most pronounced for negative acids, and least pronounced for uncharged non-oxygen acids.

f) The feasibility of titration of a certain acid in solvents of the given potential range scale may be estimated, therefore, with an accuracy sufficient for analytical purposes, if the h.n.p. in one or two solvents with large potential ranges is known. Even the knowledge of its relative acidity in water may often suffice for this purpose.

g) Carboxylic acids (and phenols, as will be shown in a subsequent paper) have been found to yield anomalous titration curves in inert and weakly basic solvents.

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The authors are much indebted to Miss A. SNIP and Miss J. P. E. SMID, who skilfully carried out the experiments.

They wish to express their gratitude to Dr. Ir. P. N. DEGENS Jr. for his stimulating interest in this investigation.

Thanks are due to the Management of the Koninklijke/Shell-Laboratorium, Amsterdam for permission to publish this paper.

SUMMARY

The present study was aimed at finding practically applicable criteria for choosing suitable conditions for potentiometric titration of acids and bases in non-aqueous solvents.

To this end the acidity potential ranges of twelve solvents of widely varying properties, and the half-neutralization potentials (h.n.p.'s) in these solvents of sixteen acids of various types (including protonated bases), were determined.

For the titration of acids new, strongly basic titrant solutions were developed, consisting of tetra-alkylammonium bases dissolved in pure pyridine.

RÉSUMÉ

Le but de la présente étude a été de trouver des critères pratiquement applicables pour le choix de conditions appropriées au titrage potentiométrique d'acides et de bases dans des solvants non-aqueux.

A cette fin les auteurs ont déterminé les domaines d'acidité de douze solvants, ayant des propriétés très divergentes, ainsi que les potentiels de demi-neutralisation (h.n.p.) dans ces solvants de seize acides de type différents, y compris des bases protonées.

Pour le titrage des acides de nouvelles solutions étalon fortement basiques ont été préparées, composées de bases de tétra-alkylammonium dissoutes dans la pyridine pure.

ZUSAMMENFASSUNG

Das Ziel des in der vorliegenden Arbeit beschriebenen Studiums war, praktisch brauchbare Normen für die Wahl geeigneter Bedingungen für die potentiometrische Titration von Säuren und Basen in nichtwässrigen Lösungsmitteln zu finden.

Dazu wurden die Aziditätspotentialbereiche von zwölf Lösungsmitteln mit sehr verschiedenen Eigenschaften und die Halbneutralisationspotentiale (half-neutralization potentials, h.n.p.'s) in diesen Lösungsmitteln von sechzehn Säuren verschiedener Art (darunter protonierte Basen) bestimmt.

Für die Titration von Säuren wurden neue, stark basische Titrierlösungen entwickelt, die aus in reinem Pyridin gelösten Tetraalkylammoniumbasen bestehen.

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POTENTIOMETRIC TITRATIONS IN NON-AQUEOUS SOLUTION

II. ANOMALOUS BEHAVIOUR OF WEAK OXYGEN ACIDS IN INERT AND WEAKLY BASIC SOLVENTS

by

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INTRODUCTION

For the diagrams of half-neutralization potentials (h.n.p.'s) given in the preceding paper[1] it had been the intention to make extensive use of carboxylic acids and phenols. Their general level of acidity, their great variety, easy availability and practical importance seemed to render these acids ideal test objects for our hypotheses. It soon appeared, however, that an accurate determination of the h.n.p.'s of these compounds in inert and weakly basic solvents presents severe difficulties. As the observed anomalies are important from an analytical point of view, and interesting in a physicochemical respect, the factors of influence on their occurrence have been established.

DESCRIPTION OF THE ANOMALIES

The abnormal course of the neutralization of the carboxylic acids and phenols in inert and weakly basic solvents manifested itself by four types of anomalies in the titration curves, occurring either separately or in combination:

a) Additional potential rise at half-neutralization

In addition to the normal potential rise at the equivalence point the titration curve showed a rise in the region of half-neutralization (Fig. 1a, Fig. 2a).

b) Non-symmetric plateau ("Hunch")

The titration curve possessed a plateau non-symmetric with respect to the point of half-neutralization. The curve was often rounded off in its first half to a distinct "hunch" (Fig. 1b, c, Fig. 4d).

c) Non-reproducibility of the curves

Duplicate titration curves, possessing either an additional potential rise or a "hunch", were shifted over considerable distances relative to each other, the dif-

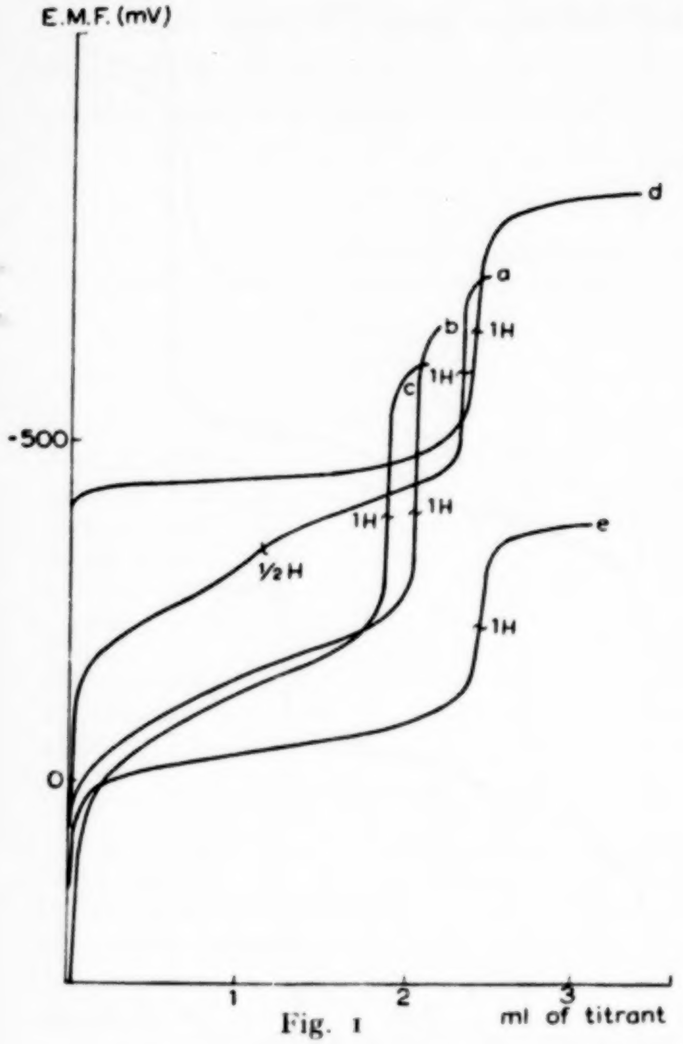


Fig. 1

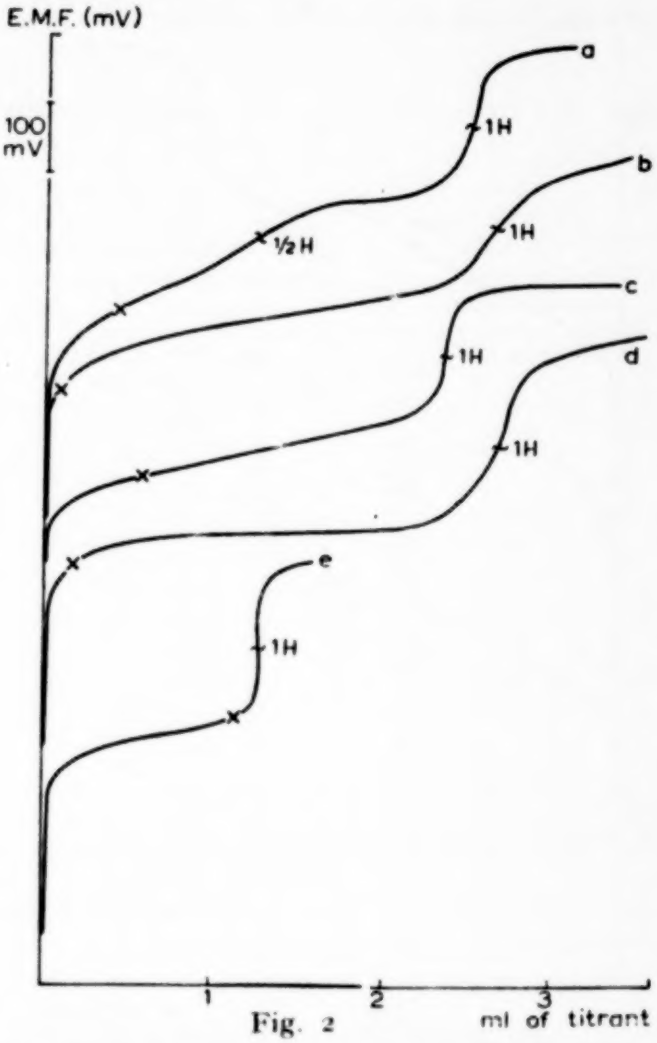


Fig. 2

Fig. 1. The influence of the solvent on the titration curves of carboxylic acids

Curve	*Solute*	*Solvent*	*Titrant*	*Electrodes*
a	Acetic acid	Acetone	Bu_3MeNOH in pyr.	Glass-calomel
b	Acetic acid	Acetonitrile	Bu_3MeNOH in pyr.	Glass-calomel
c	Acetic acid	Chlorobenzene	Bu_3MeNOH in pyr.	Glass-calomel
d	Acetic acid	*n*-Butylamine	Bu_3MeNOH in pyr.	Glass-calomel
e	Acetic acid	I.P.A.	Bu_3MeNOH in I.P.A.	Glass-calomel

I.P.A. = Isopropyl alcohol

Fig. 2. The influence of various factors on the titration curves of phenolic compounds

Curve	*Solute*	*Solvent*	*Titrant*	*Electrodes*
a	Phenol	Pyridine	Bu_3MeNOH in pyr.	Glass-calomel
b	Phenol	E.D.A.	Bu_3MeNOH in pyr.	Glass-calomel
c	Phenol	Pyridine	Bu_3MeNOH in I.P.A.	Glass-calomel
d	4Me-2.6-*t*-Bu-1-phenol	Pyridine	Bu_3MeNOH in pyr.	Glass-calomel
e	Thiophenol	Acetonitrile	Bu_3MeNOH in pyr.	Glass-calomel

× Denotes —500 mV except in curve e, where it denotes —200 mV
E.D.A. = Ethylene diamine
I.P.A. = Isopropyl alcohol

ference in potential between corresponding points in the titrations sometimes amounting to as much as 150 mV (Fig. 4a, c).

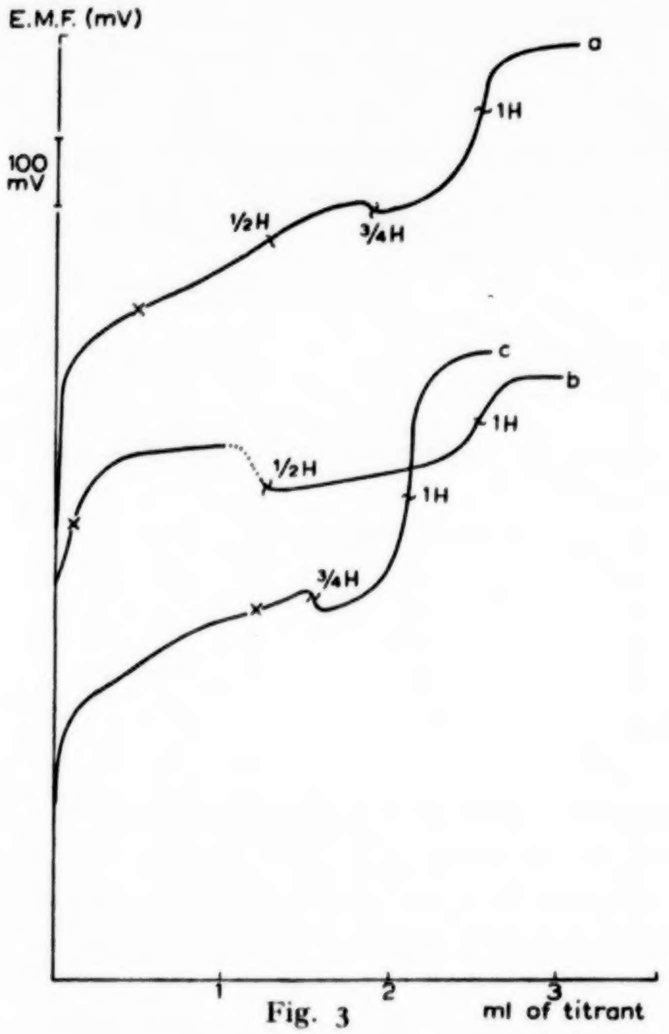


Fig. 3

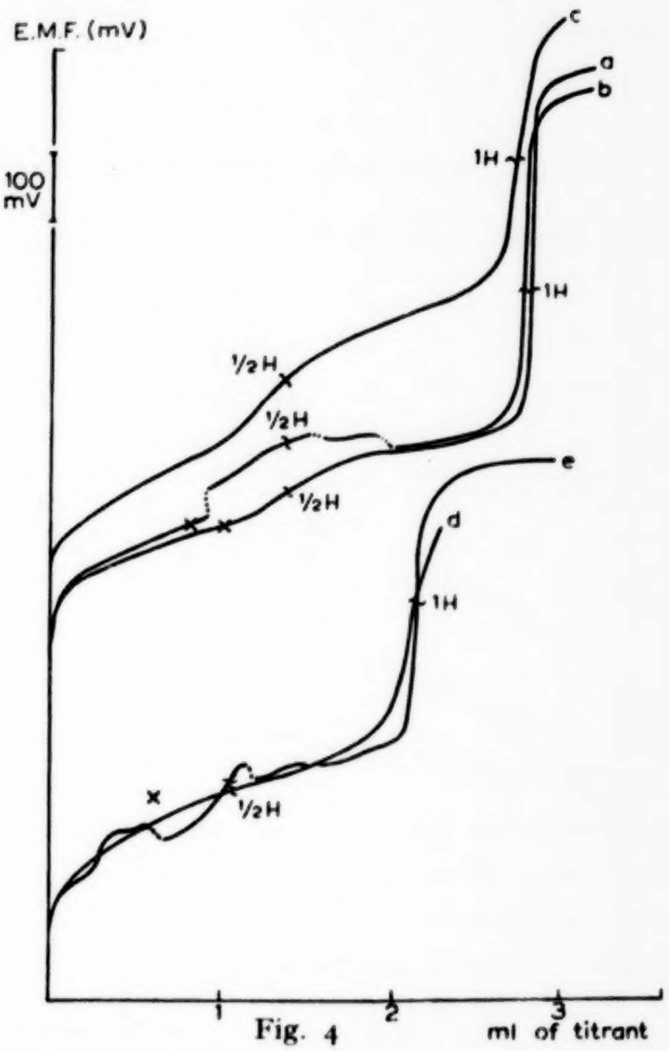


Fig. 4

Fig. 3. Potential drops in titration curves of associating acids

Curve	*Solute*	*Solvent*	*Titrant*	*Electrodes*
a	Phenol	Pyridine	Bu_3MeNOH in pyr.	Glass-calomel
b	Cetyl phenol	*n*-Butylamine	Bu_3MeNOH in pyr.	Glass-calomel
c	Benzoic acid	Acetonitrile	Me_4NOH in pyr.	Antimony-calomel

× Denotes —500 mV

Fig. 4. Anomalous titration curves of associating acids

Curve	*Solute*	*Solvent*	*Titrant*	*Electrodes*
a b c	Formic acid	Acetone	Me_4NOH in pyr.	Glass-calomel
d	*p*-Toluene Sulphinic acid	Acetonitrile	Bu_3MeNOH in pyr.	Glass-calomel
e		Acetone	Bu_3MeNOH in pyr.	Glass-calomel

× Denotes 0 mV

d) Potential drops at stages of the titration corresponding to simple fractions of total neutralization

The titration curves often showed not only the potential rise at half-neutralization but also steep potential drops, generally at points corresponding to other simple fractions of neutralization (*e.g.* at $\frac{1}{4}$, $\frac{1}{2}$, or $\frac{3}{4}$ neutralization) (Fig. 3a, b, c).

In other instances stray "ups-and-downs" occurred at various stages of the titration (Fig. 4b, e).

Table I gives a survey of the results obtained.

TABLE I

POTENTIOMETRIC TITRATIONS OF ASSOCIATING ACIDS. OCCURRENCE OF ANOMALIES IN TITRATION CURVES

	Chlorobenzene	*Acetone*	*Acetonitrile*	*Water Methyl alc. Isopropyl alc.*	*Dimethylform.*	*Pyridine*	*n-Bu-amine*	*Ethylene diamine*
Formic acid		½↑; ↑↑↓↓	½↑	N	½↑	N		
Salicylic acid		H	H	N	N	N		N
Benzoic acid	H	½↑	H; ¾↓	N	N	N	N	N
Acetic acid	H	½↑	H	N	½↑	N	N	N
p-Toluenesulphinic acid		↑↑↓↓; ½↑	H	N		N		
Phenol	½↑		H		½↑; A	½↑; ¾↓	N	N
Cetylphenol			H		½↑; A	H	½↓	N
Thiophenol		N	N	N	A	N		
4-Me-2.6-*t*-Bu-1-phenol		N	N		A	N		

N = normal
H = hunch
½↑ = potential rise at half-neutralization
½↓; ¾↓ = potential drop at half-neutralization or ¾ neutralization
↑↑↓↓ = irreproducible "ups and downs"
A = anomalous in another way

INTERPRETATION OF THE ANOMALIES, EXPERIMENTAL EVIDENCE

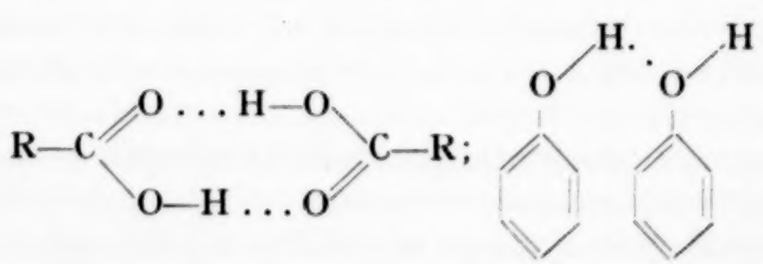
Although the phenomena described under *a*) and *b*) differ from those mentioned under *c*) and *d*) as to their immediate cause, the underlying principle is the same in all instances.

In the authors' opinion, all of the anomalies are due to the insufficient shielding (solvation) of the highly polar acid molecules and their ions by the inert or weakly basic solvents. This insufficient solvation gives rise to acid-anion association and acid dimerization, which cause the anomalies mentioned under *a*) and *b*), and to adsorption of solutes on to the electrode surfaces, which is responsible for the anomalies reported under *c*) and *d*).

a), *b*) *Acid-anion association and acid dimerization as causes of additional potential rises and asymmetrical plateaus*

The dimerization of carboxylic acids and phenols in non-polar solvents has already formed the subject of many investigations[2,3,4].

The acid molecules are known to be held together by hydrogen bonds:



It has been reported[4], however, that in weakly polar solvents having some proton-accepting tendency such acid dimerization does not occur. During titration with a base, on the other hand, the corresponding anions are formed, which are intrinsically stronger bases than the corresponding acids. It will therefore be understood that even in solvents in which acid dimerization does not occur, acid-anion association will take place. Recently evidence has been obtained for the existence of acid-anion complexes in non-polar solvents such as benzene and chloroform[5,6,7]. This is probably the first time, however, that a clear indication of the existence of such complexes even in polar and distinctly basic solvents has been obtained from potentiometric data. It is interesting to note that curves identical to those obtained in the present investigation were predicted from theoretical calculations by RICCI[8] for "pseudo-dibasic acids", though this author only considered aqueous solutions, in which they are not likely to occur.

Evidence for the validity of our interpretation of the anomalies described under *a*) and *b*) is provided by the fact that the occurrence of these anomalies was found to be counteracted by:

1. Basicity of the solvent,
2. Amphiprotic character of the solvent,
3. Steric hindrance in the acid molecule,
4. Substitution of –OH in phenols by –SH.

Additional evidence is supplied by the fact that analogous anomalies were encountered in the case of:

5. Substitution of –COOH in carboxylic acids by –SOOH.

Inconclusive evidence was obtained only as regards the expected adverse effect on the occurrence of the anomalies exerted by:

6. Internal hydrogen bonding in the acid molecule.

Re 1. The effect of the basicity of the solvent

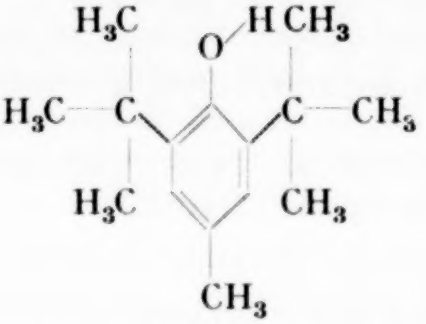
If the ratio between basicity of solvent and basicity of acid anion exceeds a certain critical value, the acid molecules will associate with the solvent rather than with their own anions. Thus the moderately strong carboxylic acids yielded anomalous curves in all non-acidic solvents of weaker basicity than pyridine. In the latter solvent, and in more strongly basic ones, normal curves were obtained. For the much weaker acidic phenols the limits of occurrence of the anomalies lie at much higher basicities, normal curves being obtained in *n*-butylamine and ethylene diamine only (*cf.* Fig. 1a, b, c, d, and Fig. 2a, b).

Re 2. The effect of the amphiprotic character of the solvent

The amphiprotic solvents possess excellent solvating properties as they are both proton acceptors and proton donors. In their presence the tendency of the dissolved acid to form complexes with its own anions will be greatly decreased. No trace of anomalous behaviour was observed in the alcoholic solvents, or in water (*cf.* Fig. 1e). Even the presence of small amounts of isopropyl alcohol appeared to be sufficient to suppress the extra inflection of phenol in pyridine (*cf.* Fig. 2c).

Re 3. The effect of steric hindrance in the acid molecule

The fact that 4-Me-2,6-*t*-Bu-1-phenol:



though having approximately the same acidity as phenol, yields a normal titration curve in solvents in which phenol produces a marked additional inflection, is perhaps one of the most striking evidences for the validity of our interpretation (Fig. 2d). It may be mentioned that under the same conditions 4-Me-2-*t*-Bu-1-phenol did show the anomalous rise at half-neutralization.

Re 4. The effect of substitution of –OH in phenol by –SH

Thiophenol yielded normal curves even in a very weakly basic solvent such as acetonitrile (Fig. 2e). This is in complete agreement with the known fact that sulphur, in contrast to oxygen, has little tendency to act as an acceptor in hydrogen bonding.

Re 5. The effect of substitution of –COOH in carboxylic acids by –SOOH

The configuration of the carboxylic acids is found in many other acids, such as the sulphinic acids, RSO_2H, the arsinic acids R_2AsO_2H, and the phosphinic acids R_2PO_2H. The behaviour of *p*-toluenesulphinic acid $CH_3C_6H_4.SO_2H$ was found to be quite analogous to that of the carboxylic acids (Fig. 4d, e).

Re 6. The effect of internal hydrogen bonding in the acid molecule

Some indications were obtained suggesting an adverse effect of internal hydrogen bonding, such as exists in salicylic acid and *o*-nitrophenol, on the occurrence of the anomalies. They were not sufficiently evident to warrant presentation.

All these observations are in agreement with the interpretation advanced above. As not one piece of evidence obtained was inconsistent with our assumptions, there seems to be little reason to doubt their validity.

c), d) Adsorption of solutes on to the electrode surfaces as a cause of the irreproducibility of titration curves and of the occurrence of potential drops

The tendency of polar solutes to adsorb on to polar surfaces is a much studied phenomenon for details of which the reader is referred to the handbooks of surface chemistry. The specific effects on potential measurements in inert solvents have, to our knowledge, not previously been observed. Reference may, however, be made to a recent observation of BODAMER AND KUNIN[9], who found that carboxylic acids are taken up from non-polar solvents by strongly basic anion exchangers in amounts far exceeding those corresponding to the normal capacity of the latter.

Experimental evidence from the present investigation, supporting the interpretation of the anomalies mentioned under *c*) and *d*), is given by:

1. The non-equilibrium character of the titrations,
2. The occurrence of potential drops at stages of the titration corresponding to simple fractions (*e.g.* $\frac{1}{4}$, $\frac{1}{2}$, $\frac{3}{4}$) of total neutralization,
3. The effect of the type of electrodes used on the occurrence of the anomalies,
4. The preferential crystallization at the electrode surfaces occurring whenever an insoluble salt is formed during the titration.

Re 1. The non-equilibrium character of titration

The character of the curves, in particular the sudden potential drops, proves beyond doubt that the systems are not permanently in equilibrium. As all the solutions were homogeneous, containing no precipitate or turbidity, there seems to be little reason to suppose that the establishment of equilibrium in the solution would be in any way impeded. It should further be noted that the potentials measured were generally stable, except in a few cases in certain phases of the titration.

The origin of the non-equilibrium character of the titration therefore presumably lies at the surfaces of the electrodes. It seems plausible that acid molecules or ions or complexes will tend to adsorb on to these highly polar surfaces. According to what species is preferentially adsorbed, and is therefore present in increased concentration at the interface, the measured potentials will lag behind or be ahead of those of the bulk of the solution. The observed irreproducibility of the curves is in agreement with the supposed adsorption, as the latter will be much dependent upon the previous history of the electrodes.

Re 2. The occurrence of potential drops at stages of the titration corresponding to simple fractions of total neutralization

The circumstance that the potential often drops at stages of the titration where a simple fraction (*e.g.* $\frac{1}{4}$, $\frac{1}{2}$, $\frac{3}{4}$) of the acid has been neutralized is understandable, as at these stages the equivalence point of one complex is reached while the newly formed complex may well possess other adsorbability characteristics.

Re 3. The effect of the type of electrodes on the occurrence of anomalies

The occurrence of the anomalies was found to be dependent upon the type of electrodes, particularly of the indicator electrode, used. Thus a titration which had been found to proceed in a quite irreproducible manner with the glass electrode (*cf.* Fig. 4a, b) yielded reproducible curves (without potential drops) when carried out with the platinum indicator electrode.

The titration of benzoic acid in acetonitrile, on the other hand, yielded a potential drop at $\frac{3}{4}$ neutralization with the antimony indicator electrode (Fig. 3c), but not with the glass electrode.

In view of the irreproducibility of these phenomena a statistical treatment would be required for the unequivocal establishment of their dependence upon the electrodes used.

References p. 400

Re 4. The preferential crystallization of precipitates on the electrode surfaces whenever an insoluble salt is formed

If during titration in an inert or weakly basic solvent a precipitate is formed, the latter is often observed to adhere to the electrode surfaces. This crystallization seems to be the macroscopic extension of a primary microscopic adsorption.

CONCLUSIONS

1. The observed influence of some characteristics of solvent and dissolved acid, and that of the type of electrodes used on the occurrence of anomalous titration curves of a number of carboxylic acids, phenols and related compounds, support the assumption that the anomalies are caused by acid-anion association and by adsorption of solutes on to the electrode surfaces.
2. The results imply that solvents to be used for differentiating titrations of weak acids are to be chosen with great care. On the one hand the wish for maximum differentiation would lead one to choose as inert a solvent as is compatible with the requirements set by solubility and conductivity. On the other hand, the very feature of inertness, *i.e.* of non-interaction with the dissolved acids and their products of neutralization, drives the latter together and to the electrode surfaces, thereby spoiling much or all of the beneficial effect of such solvents.

It is the author's experience that in practical applications it often takes very sharp sailing between the Scylla of levelling and the Charybdis of hydrogen bond complex formation to obtain optimal separation of mixtures of weak acids. Nevertheless, the importance of such differentiating determinations for industrial purposes often justifies considerable effort.

ACKNOWLEDGEMENT

The author is much indebted to Miss A. SNIP AND Miss J. P. E. SMID, who have skilfully carried out the experiments.

He wishes to express his gratitude to Dr. Ir. E. A. M. F. DAHMEN for his stimulating interest in this investigation.

Thanks are due to the Management of the Koninklijke/Shell-Laboratorium, Amsterdam for permission to publish this paper.

SUMMARY

A number of carboxylic acids, phenols and certain related compounds have been found to yield anomalous titration curves in inert and weakly basic solvents. Amongst the effects observed are reproducible potential rises in the region of half-neutralization and irreproducible potential drops often at stages of the titration corresponding to simple fractions of total neutralization.

An investigation has been made into the influence of the basic and amphiprotic character of the solvents, of steric hindrance in the acid molecules, of substitution of $-OH$ (in phenols) by $-SH$, and of $-COOH$ (in carboxylic acids) by $-SOOH$, and of the type of electrodes on the occurrence and type of anomalies.

These, and the other observed anomalies are interpreted.

RÉSUMÉ

Titrés par potentiométrie dans des solvants inertes ou faiblement basiques, un certain nombre d'acides carboxyliques, de phénols et d'autres composés de même nature donnent des courbes anormales. Parmi les effets observés, on remarque des augmentations de potentiel reproductibles dans la région de demi-neutralisation et des chutes de potentiel non-reproductibles qui se présentent souvent à des points correspondant à des fractions simples de la neutralisation totale.

Une étude a été faite sur la façon dont les phénomènes observés sont influencés par le caractère basique et amphiprotique des solvants, l'empêchement stérique dans les molécules acides, la substitution du groupement –OH (dans les phénols) par –SH, et du groupement –COOH (dans les acides carboxyliques) par –SOOH, et le type des électrodes appliquées.

L'auteur explique le comportement anormal signalé.

ZUSAMMENFASSUNG

Es hat sich herausgestellt, dass eine Anzahl von Carboxylsäuren, Phenolen und bestimmten verwandten Verbindungen in inerten und schwachbasischen Lösungsmitteln abnormale Titrationskurven liefern. Nebst anderen Effekten wurden reproduzierbare Potentialanstiege im Gebiet der Halbneutralisation und nichtreproduzierbare Potentialabfälle beobachtet, oft an einfachen Fraktionen der Totalneutralisation entsprechenden Stellen.

Es wurde untersucht welchen Einfluss der basische und amphiprotische Charakter der Lösungsmittel, sterische Hinderung in den Säuremolekeln, Substitution von –OH (in Phenolen) durch –SH und von –COOH (in Carboxylsäuren) durch –SOOH, sowie die Art der Elektroden auf Vorkommen und Art der Anomalien hat.

Diese und die anderen Anomalien werden erklärt.

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NEW SUBSTITUTED 2,2'-DIPYRIDINES AND THEIR CHELATION AS Fe(II) AND Cu(I) COMPLEX CATIONS

by

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INTRODUCTION

More than 150 substituted 1,10-phenanthrolines, dipyridines, tripyridines and diquinolines have been synthesized; spectrophotometric studies of their Fe(II), Cu(I) and Co(II) chelation complexes have been made. Many valuable analytical applications have been devised, and are widely employed in trace element determinations of iron and of copper in foods, feeds, wine, ferrous and non-ferrous alloys, paper, and biological materials. Among the metals which form similar, but colorless chelation complexes with these types of heterocyclic ring nitrogen compounds are Cd, Ni, Zn, and Mn.

All these ferroine, terroine and cuproine chelation reagents are noted for their color specificity, sensitivity, and stability. The wide range of permissible pH tolerance contributes to their wide versatility. A pH range of 1 or 2 to, and including pH 9 and 10 is generally operative. Some types are applicable to very strong alkaline media with full color development and permanent color stability. The ferrous complex cations of many types serve as valuable oxidation-reduction indicators which are of favorable color transition, reversibility, and potential range. Types are available covering a series of redox potentials from 0.88 volts to 1.25 volts in steps of 0.01 to 0.02 volts. Other applications involve their use as masking reagents and selective anion precipitants.

No other known type of organic analytical reagent provides an equal number of possible substitution derivatives which leads to singularly important structure modulations precisely predictable in property prognosis.

The present work describes the spectrophotometric constants of 4,4'-diphenyl-, and diamino-2,2'-dipyridines. It has been found that both these substituted derivatives of ferroine and cuproine reacting dipyridines have properties favorable to practical quantitative applications. Comparison classification with a series of substituted di-, and tripyridines is provided to bring out predictable synthetic substituent group alterations governing their resultant spectrophotometric constants.

PREVIOUS STUDIES

The study of the influence of CH_3, C_2H_5, C_6H_5, NO_2, NH_2, OCH_3, Cl, Br, and OH groups as substitutions for the various hydrogen atoms in 1,10-phenanthroline, 2,2'-dipyridine and diquinoline as well as in 2,2',2''-tripyridine, has been extensively studied. The investigations disclose that the phenyl-, amino-, and hydroxy substitutions in the parent molecule for the 4,7 and the 2,9 hydrogens of 1,10-phenanthroline exert maximum alterations in spectrophotometric constants. The same group substitutions react similarly when provided for the hydrogen atoms *ortho* and *para* in position with respect to nitrogen in the above remaining three type ligands.

In the selection of proposed substituted 2,2'-dipyridines, therefore, the choice was made of 4,4'-diphenyl-2,2'-dipyridine and the similarly substituted diamino-derivative. The spectrophotometric constants of a series of substituted di- and tripyridines including the diphenyl-, and diamino types not previously described, are given in Tables I and II.

TABLE I

2,2'-DIPYRIDINE AND ITS SYMMETRICAL DISUBSTITUTED DERIVATIVES IN CHELATION WITH Cu(I) AND Fe(II)

2,2'-Dipyridine	*Fe(II) chelation*		*Cu(I) chelation*	
	λ_{max} *in mμ*	ε	λ_{max} *in mμ*	ε
Unsubstituted	522	8650	435	4550
4,4'-Dimethyl-	526	8470	433	5210
6,6'-Dimethyl-	—	—	455	6570
4,4'-Diphenyl-	386 and 552	21360 and 21280	463	9600
4,4'-Diamino-	379 and 569	13640 and 8135	faintly complexed only	
4,4',6,6'-Tetramethyl-	—	—	450	6800

The first three dipyridines of Table I have been previously described[1]. The last three are herein described for the first time.

TABLE II

2,2',2''-TERPYRIDINE AND ITS SUBSTITUTED DERIVATIVES IN CHELATION WITH Co(II) AND Fe(II)

Terpyridine	*Fe(II) chelation*		*Co(II) chelation*	
	λ_{max} *in mμ*	ε	λ_{max} *in mμ*	ε
Unsubstituted	552	12500	444 and 506	1420 and 1240
4'-Phenyl-	569	22185	452 and 517	2630 and 2690
4,4''-Dimethyl-4'-phenyl-	575	26360	457 and 519	2440 and 2514
4,4',4''-Triphenyl-	383 and 583	21100 and 30200	466 and 528	3050 and 3120
6,4',6''-Triphenyl-	—	—	423 and 567 (Cu (I) chelation)	4520 and 3180

The first four ligands of Table II having the trivial names, tripyridine, terosole, terosine, and terosite[2,3] have been previously described. The last triphenyl substituted terpyridine is for the first time herein characterized. It does not chelate with Fe(II) or Co(II) and is poor in Cu(I) chelation. A detailed description of its properties is therefore omitted. The chemical name is 2,6-bis(6-phenyl-2-pyridyl)-4-phenylpyridine.

From an examination of the data of Tables I and II it is to be observed that the substitution of methyl, amino, and phenyl groups, for the 4,4',4'' positioned hydrogen atoms of both di- and tripyridine has progressively and materially altered the wavelength of maximum absorption λ, and the molar absorbtivity ε. The single exception in Fe(II), Cu(I) and Co(II) chelation is that of 4,4'-dimethyl-2,2'-dipyridine in the case of the ferrous iron complex. The same general result has been observed for similar substitutions in the 4,7-position in 1,10-phenanthrolines in Fe(II) and Cu(I) reactions. The substitution of methyl groups in the 6,6'-position in 2,2'-dipyridine is effective in preventing Fe(II) chelation but provides Cu(I) chelation (more favorable in comparison with diquinoline), having methyl substitutions adjacent to the nitrogens.

A further study of 4,4'-diphenyl- and diamino-2,2'-dipyridines is appropriate, and is herein provided.

CHELATION PROPERTIES OF 4,4'-DIPHENYL-2,2'-DIPYRIDINE AS THE FERROUS COMPLEX

The ferrous complex of this new ligand forms in aqueous media at pH range 1.9 to 9.4; rapid and complete chelation occurs in the pH range 3.1 to 8.8. The water insoluble complex is soluble in ethanol and aqueous ethanol and in *iso*amyl alcohol. The insoluble ferrous complex is readily and quantitatively extracted employing *iso*amyl alcohol.

Weighed samples of standard iron solution were placed in 25 ml volumetric flasks and reduced by the addition of 2 ml of 10 % hydroxylamine solution. An acetate buffer solution (pH 5.8, 5 ml). and 2.0 ml of $0.01\,M$ chelation reagent were then added followed by ethanol to dilute to volume. The solutions were examined by comparison with a reagent blank employing a Cary Recording Spectrophotometer, Model 11, with matched 10 mm silica cells.

The results are recorded in data of Table III. The standard iron solution contained 0.0001163 g per gram. The color stability was proven by storage for seven months with no diminution in value.

TABLE III

SPECTROPHOTOMETRIC DATA FOR 4,4'-DIPHENYL-2,2'-DIPYRIDINE AS THE Fe(II) COMPLEX

Fe solution	*Absorbance*		*Molar absorbtivity*	
g	*552 mμ*	*386 mμ*	*552 mμ*	*386 mμ*
0.3982	0.700	—	21110	—
0.4955	0.872	—	21130	—
0.6034	1.064	—	21170	—
0.6541	1.157	—	21240	—
0.7438	1.304	—	21050	—
0.8083	1.480	1.437	21990	21360
			Av 21282	

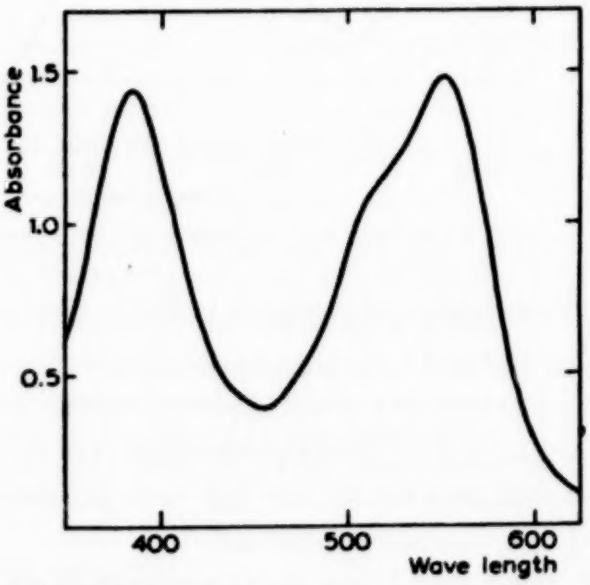

Fig. 1. Spectrophotometric absorption curve of 4,4'-diphenyl-2,2'-dipyridine as the ferrous complex.

A graph of the absorption spectrum is reproduced in Fig. 1.

CHELATION PROPERTIES OF 4,4'-DIPHENYL-2,2'-DIPYRIDINE AS THE CUPROUS COMPLEX

The same procedure in the preparation of the cuprous complex of the 4,4'-phenyl substituted chelate was employed as in the case of the corresponding ferrous complex, replacing iron by copper. It was found that the cuprous complex is exceptionally unstable and is oxidized when in contact with atmospheric oxygen at a rate in excess of that operative in the reduction of copper by hydroxylamine. The spectrophotometric constants shown in Table I were obtained by a process of rigid exclusion of oxygen. The instability of the cuprous complex precludes practical application in the trace analytical determination of copper.

4,4'-DIAMINO-2,2'-DIPYRIDINE

This substituted diamino-dipyridine as the hydrochloride is soluble in water. Only the Fe(II) complex of this ligand was studied, as the Cu(I) complex is of insufficient color intensity to call for further study. Color stability may be shown in the pH range of 4 to 14 for the Fe(II) complex.

Spectrophotometric constants were determined by a procedure duplicating that for the 4,4'-diphenyl-2,2'-dipyridine. The use of aqueous ethanol was required to maintain the ferrous complex soluble. Extraction of the complex employing *iso*amyl alcohol is not complete except by 3 consecutive applications. The aqueous ethanol solutions of the complex were subjected to spectrophotometric examination and the data are found in Table IV. The ligand was added in the form of its 0.01*M* solution in water.

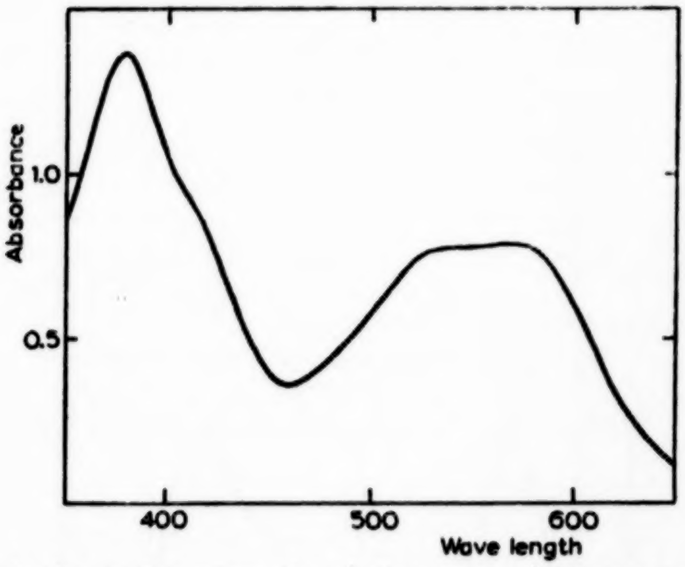

Fig. 2. Spectrophotometric absorption curve of 4,4'-diamino-2,2'-dipyridine as the ferrous complex.

The spectrophotometric recorded absorption characteristics are shown in Fig. 2. By examination of the data in Table IV and its spectrophotometric recording, it will be observed that the values of the molar absorbtivities found are not outsanding when compared to the corresponding 4,4'-diphenyl analogue. Also only one of the absorption peaks is sharply defined at variance to the case for both peaks observed in Fig. 1 for the phenyl substituted ligand.

4,4'-DIAMINO-2,2'-DIPYRIDINE AS AN ACTIVE REDUCTANT

A noteworthy property of this ligand consists in its effectiveness in the reduction of

TABLE IV

THE Fe(II) COMPLEX OF 4,4′-DIAMINO-2,2′-DIPYRIDINE
(STANDARD IRON SOLUTION 0.0001163 g PER g)

Fe solution	*Absorbance*		*Molar absorbtivity*	
g	*379 mμ*	*569 mμ*	*379 mμ*	*569 mμ*
0.3952	0.450	0.272	13670	8264
0.7229	0.844	0.500	14020	8305
0.9785	1.102	0.670	13520	8222
1.2239	1.360	0.790	13340	7751
			Av. 13637	Av. 8135

ferric to ferrous iron. The procedure previously described in the formation of its Fe(II) complex without the addition of hydroxylamine shows spectrophotometric absorption duplicating that shown in Fig. 2. The composition of the oxidized form of the amino-ligand was not further investigated.

The newly herein described 4,4′-diamino- and diphenyldipyridines were synthesized by Professor FRANCIS CASE and associates at Temple University, Philadelphia. A detailed description of their synthesis will appear later. The 4,4′,6,6′-tetramethyl-2,2′-dipyridine was prepared by Doctor ROBERT H. LINNELL and a detailed description of its synthesis will be published elsewhere.

SUMMARY

A study has been made of three new substituted 2,2′-dipyridines, the 4,4′-diphenyl- and diamino-dipyridines and 4,4′,6,6′-tetramethyldipyridine. Comparison is made between their chelation properties as Fe(II) and Cu(I) colored complexes with similarly substituted di- and tripyridines previously described.

4,4′-Diphenyl-2,2′-dipyridine forms a ferrous complex of exceptionally large molar absorbtivity (21300), and which has two widely separated absorption maxima (386 and 552 mμ) and equal sensitivity at both absorption peaks. The Cu(I) complex is very sensitive to oxidation in contact with air.

4,4′-Diamino-2,2′-dipyridine is noteworthy because of its ability to reduce Fe(III) to Fe(II).

RÉSUMÉ

Une étude a été effectuée sur trois nouvelles 2,2′-dipyridines substituées: les 4,4′-diphényl- et diaminodipyridines et la 4,4′,6,6′-tétraméthyldipyridine. Une comparaison est faite entre les propriétés des complexes colorés du fer(II) et du cuivre(I) de ces composés et celles des complexes obtenus avec des di- et tripyridines déjà étudiées. La 4,4′-diphényl-2,2′-dipyridine donne un complexe de fer(II) présentant un coefficient d'extinction moléculaire (21300) extraordinairement élevé, deux maxima d'absorption très éloignés (386 et 552 mμ) et une sensibilité égale pour chaque maximum. Le complexe du cuivre(I) est très oxydable à l'air. La 4,4′-diamino-2,2′-dipyridine est intéressante par le fait qu'elle peut réduire Fe(III) en Fe(II).

ZUSAMMENFASSUNG

Drei neue substituierte 2,2′-Dipyridine, die 4,4′-Diphenyl- und Diaminodipyridine und das 4,4′-6,6′-Tetramethyldipyridin wurden untersucht. Die Eigenschaften ihrer gefärbten Komplexverbindungen mit Fe(II) und Cu(I) wurden mit denjenigen von ähnlich substituierten Di- und Tripyridinen verglichen.

Das 4,4′-Diphenyl-2,2′-dipyridin bildet einen Ferro-Komplex mit einem aussergewöhnlich grossen molaren Extinktionskoeffizienten (21300), zwei weit von einander entfernten Absorptionsmaxima und gleicher Empfindlichkeit bei beiden Absorptionsspitzen. Der Cu(I)-Komplex ist an der Luft sehr empfindlich gegen Oxydation. Das 4,4′-Diamino-2,2′-dipyridin ist interessant da es Fe(III) zu Fe(II) zu reduzieren vermag.

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ÜBER DIE TRENNUNG ANORGANISCHER STOFFGEMISCHE DURCH VERTEILUNG

14. MITTEILUNG[1]. DIE VERTEILUNG VON POLYJODIDEN ZWISCHEN WÄSSRIGEN LÖSUNGEN UND ORGANISCHEN LÖSUNGSMITTELN

von

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ALLGEMEINES

Nach DAWSON[2-4] können die Polyjodide der Alkalimetalljodide sowie des Ammoniumjodids und des Tetramethylammoniumjodids aus wässrigen Lösungen mit Nitrobenzol und Äthylacetat ausgeschüttelt werden; nach SAKELLARIDIS[5] gehen die Trijodide des Natriums, Kaliums und Rubidiums bei der Verteilung in Diäthyläther, Ammoniumtrijodid auch in Benzol[6].

Da es nicht ausgeschlossen erschien, dass auf Grund dieser Verteilungsreaktionen analytische Trennungsmethoden für die Alkalimetalle ausgearbeitet werden konnten, wurden die betreffenden Systeme ausführlicher untersucht. Besonders eingehend wurde dabei das Verhalten der Polyjodide von Kaliumhalogeniden geprüft; es ist anzunehmen, dass die Halogenide der anderen Alkalimetalle sich im Prinzip ähnlich verhalten.

Die angegebenen Verteilungskoeffizienten sind definiert als

$$a = \frac{\text{Konzentration in der organischen Schicht}}{\text{Konzentration in der Wasserschicht}}$$

Aus diesen wurde die prozentuale Verteilung

$$P = \frac{100\ a}{1 + a}$$

berechnet[7]. Der Trennfaktor β eines Gemisches der Substanzen 1 und 2 ist definiert als

$$\beta = \frac{a_1}{a_2}$$

wobei das Verhältnis der Verteilungskoeffizienten im folgenden stets so gebildet ist, dass $\beta \geq 1$ wird.

Zur Bestimmung der Verteilungskoeffizienten löste man abgewogene Mengen der untersuchten Verbindungen in Wasser, gab Jod (und eventuelle weitere Zusätze) zu und schüttelte bei Raumtemperatur (20-23°C) fünf Minuten lang kräftig mit dem gewählten organischen Lösungsmittel aus. Verschiedentlich trennten sich die Phasen nach dem Schütteln nur schlecht; man liess dann die Gemische mehrere Stunden lang, teilweise sogar über Nacht, stehen. In allen Fällen waren die Volumina der Phasen vor dem Schütteln innerhalb der Versuchsfehler gleich. Für die Analysen wurden Anteile jeder Schicht eingedampft, die Rückstände mit Schwefelsäure abgeraucht und die Sulfate ausgewogen. Aus Nitrobenzol wurden wegen des hohen Siedepunktes die gelösten Verbindungen mit Wasser ausgeschüttelt, nachdem das Jod mit SO_2 reduziert worden war.

Literatur S. 415

UNTERSUCHUNG VERSCHIEDENER VARIABLER BEI DER VERTEILUNG VON POLYJODIDEN

Orientierende Verteilungsversuche mit *verschiedenen organischen Lösungsmitteln* sind in Tab. I wiedergegeben; dabei wurde einheitlich eine Konzentration von 2.0 g KJ und 10.0 g J_2 in 100 ml wässriger Ausgangslösung innegehalten (das Jod ging allerdings erst nach Zugabe der organischen Phase völlig in Lösung; es wurde jedoch hier, wie auch bei allen weiteren Versuchen, der wässrigen Lösung zugerechnet).

TABELLE I

VERTEILUNG VON KALIUMJODID-POLYJODID ZWISCHEN WÄSSRIGEN LÖSUNGEN UND VERSCHIEDENEN ORGANISCHEN LÖSUNGSMITTELN. 2.0 g KJ UND 10.0 g J_2/100 ml H_2O-PHASE. RAUMTEMPERATUR

Nr	*Organ. Lösungsmittel*	α	*P%*
1	*n*-Pentanol	7.95	88.8
2	Amylacetat	7.88	88.7
3	Diäthyläther	2.19	68.7
4	Nitromethan	8.82	89.8
5	Nitrobenzol	8.96	90.0
6	Benzol	0.009	0.9
7	Chloroform	0.005	0.5
8	Schwefelkohlenstoff	<0.001	<0.1

Die Ergebnisse stehen — mit Ausnahme von Diäthyläther — in Einklang mit den Löslichkeitsbestimmungen von DAWSON[8]; sie zeigen, dass KJ als Polyjodid mit verschiedenen organischen Flüssigkeiten ausgeschüttelt werden kann. Pentanol und Amylacetat kommen aber trotz hoher Verteilungskoeffizienten praktisch nicht in Frage, da die Systeme zum Emulgieren neigen und eine Trennung der Schichten erst nach mehrstündigem Stehen eintritt. Tetrahydrofuran, Tributylphosphat und Di-*n*-butyläther, die ebenfalls untersucht wurden, geben noch beständigere Emulsionen, sodass quantitative Ergebnisse überhaupt nicht erhalten werden konnten, während Benzol, Chloroform und Schwefelkohlenstoff nur sehr ungünstige Werte brachten. Daher wurden die weiteren Versuche hauptsächlich mit Nitromethan, das wegen des niedrigeren Siedepunktes dem Nitrobenzol vorzuziehen ist, und mit Diäthyläther durchgeführt. Von diesen erwies sich Nitromethan als besser geeignet, da beim Diäthyläther durch Bildung Gel-artiger Niederschläge verschiedentlich Störungen eintraten.

Tab. II zeigt die *Abhängigkeit der Verteilung des Kaliumjodid-Polyjodides von der J_2-Konzentration* für verschiedene KJ-Konzentrationen bei Verwendung von Diäthyl-

TABELLE II

VERTEILUNG VON KALIUMJODID-POLYJODID ZWISCHEN WÄSSRIGEN LÖSUNGEN UND DIÄTHYLÄTHER IN ABHÄNGIGKEIT VON DER J_2-KONZENTRATION. RAUMTEMPERATUR

Nr	*Wässrige Phase*		α	*P%*
	g KJ/100 ml	*g J_2/100 ml*		
1	2.0	1.0	0.014	1.4
2	2.0	2.0	0.131	11.6
3	2.0	6.0	0.879	46.8
4	2.0	10.0	2.19	68.7
5	2.0	13.0	3.19	76.1
6	20.0	2.0	0.037	3.6
7	20.0	6.0	0.144	12.6
8	20.0	10.0	0.221	18.1
9	20.0	13.0	0.309	23.6
10	20.0	20.0	0.612	38.0

Literatur S. 415

äther. Die Verteilungskoeffizienten steigen in Übereinstimmung mit den Ergebnissen von DAWSON[2] für Nitrobenzol stark mit der J_2-Konzentration an. Sie liegen bei der Versuchsreihe mit 20.0 g KJ/100 ml erheblich tiefer als bei der mit 2.0 g KJ/100 ml. Versuche mit 0.2 g KJ/100 ml waren wegen des Auftretens der erwähnten Niederschläge nur schlecht reproduzierbar und sind daher nicht mit angeführt. Aus dem gleichen Grunde wurde auch die J_2-Konzentration nicht über 13.0 g/100 ml erhöht.

TABELLE III

VERTEILUNG VON KALIUMJODID-POLYJODID ZWISCHEN WÄSSRIGEN LÖSUNGEN UND DIÄTHYLÄTHER IN ABHÄNGIGKEIT VON DER KJ-KONZENTRATION. RAUMTEMPERATUR

Nr	*Wässrige Phase*		*α*	*P%*
	g KJ/100 ml	*g J_2/100 ml*		
1	0.4	6.0	0.244	19.6
2	1.0	6.0	0.580	36.7
3	2.0	6.0	0.879	46.8
4	5.0	6.0	0.508	33.7
5	8.0	6.0	0.350	25.9
6	14.0	6.0	0.235	19.0
7	20.0	6.0	0.143	12.5
8	0.4	13.0	0.489	32.8
9	1.0	13.0	1.96	66.2
10	2.0	13.0	3.19	76.1
11	5.0	13.0	1.43	58.9
12	8.0	13.0	0.966	49.1
13	14.0	13.0	0.534	34.8
14	20.0	13.0	0.309	23.6

Der *Einfluss der KJ-Konzentration* auf die Verteilungskoeffizienten ist für verschiedene J_2-Konzentrationen und Diäthyläther als organisches Lösungsmittel in Tab. III und Abb. 1 wiedergegeben. Bei 2.0 g KJ in 100 ml wässriger Ausgangslösung wird jeweils ein Maximum der Verteilung erreicht; nach kleineren KJ-Konzentrationen sinkt der Verteilungskoeffizient schnell, nach grösseren langsamer ab. Das Nernst'sche Gesetz ist demnach in keinem Konzentrationsbereich erfüllt. Bei Verwendung von Nitromethan wurden ähnliche Kurven erhalten.

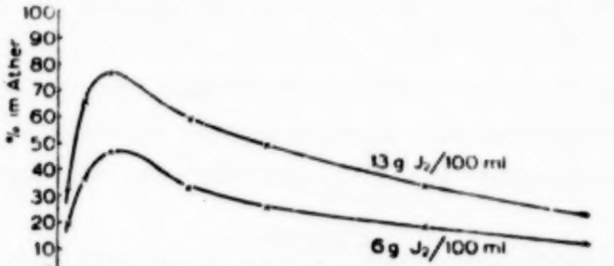

Fig. 1. Verteilung von Kaliumjodid-Polyjodid zwischen wässrigen Lösungen und Diäthyläther in Abhängigkeit von der KJ-Konzentration.

Um die *Wirkung gleichioniger Zusätze* zur Wasserschicht zu ermitteln, wurden bromwasserstoffsaure KBr-Lösungen verschiedener HBr-Konzentration mit J_2 versetzt und mit Nitromethan ausgeschüttelt. Der Verteilungskoeffizient des KBr-Polyjodids wird schon bei geringer HBr-Konzentration etwas erhöht, steigt aber nach weiterem Säurezusatz nicht mehr an.

Literatur S. 415

DIE VERTEILUNG DER POLYJODIDE DER ALKALIMETALLHALOGENIDE ZWISCHEN WÄSSRIGEN LÖSUNGEN UND NITROMETHAN IN ABHÄNGIGKEIT VON DER J_2-KONZENTRATION

Nach den obigen Versuchen ist die J_2-Konzentration der Systeme als eine der wichtigsten Veränderlichen anzusehen. Um Vergleiche zwischen Polyjodiden verschiedener Alkalimetallhalogenide ziehen zu können, wurde eine grössere Anzahl dieser Verbindungen bei variablem J_2-Gehalt, aber unter sonst gleichen Bedingungen mit Nitromethan aus wässriger Lösung ausgeschüttelt (Tab. IV-VIII). Man verzichtete darauf, in jedem einzelnen Falle das Optimum der Halogenidkonzentration zu ermitteln, sodass die Werte möglicherweise nicht völlig untereinander vergleichbar sind. Trotzdem lässt sich wohl sagen, dass die Verteilungskoeffizienten einerseits in der Reihe der Alkalimetalle vom Lithium zum Cäsium und andererseits bei dem gleichen Alkalimetall vom Chlorid zum Jodid zunehmen; nur die Fluoride fügen sich nicht in die letztere Reihe ein, sondern sind in allen untersuchten Fällen etwas besser auszuschütteln als die Chloride (vgl. auch Abb. 2 u. 3).

TABELLE IV

VERTEILUNG VON LiBr- UND LiJ-POLYJODIDEN ZWISCHEN WÄSSRIGEN LÖSUNGEN UND NITROMETHAN IN ABHÄNGIGKEIT VON DER J_2-KONZENTRATION. RAUMTEMPERATUR

Nr	*Wässrige Phase* *g Li-Verbindung pro 100 ml*	*g J_2 pro 100 ml*	α	*P%*
1	2.0 g LiBr	1.0	0.045	4.3
2	2.0 g ,,	2.0	0.051	4.9
3	2.0 g ,,	6.0	0.058	5.5
4	2.0 g ,,	10.0	0.059	5.6
5	2.0 g ,,	13.0	0.059	5.6
6	2.0 g LiJ	1.0	0.080	7.4
7	2.0 g ,,	2.0	0.222	18.2
8	2.0 g ,,	6.0	0.662	39.8
9	2.0 g ,,	10.0	0.911	47.7
10	2.0 g ,,	13.0	1.08	51.9

TABELLE V

VERTEILUNG VON NaF-, NaBr- UND NaJ-POLYJODIDEN ZWISCHEN WÄSSRIGEN LÖSUNGEN UND NITROMETHAN IN ABHÄNGIGKEIT VON DER J_2-KONZENTRATION. RAUMTEMPERATUR

Nr	*Wässrige Phase* *g Na-Verbindung pro 100 ml*	*g J_2 pro 100 ml*	α	*P%*
1	2.0 g NaF	2.0	0.017	1.7
2	2.0 g ,,	10.0	0.071	6.6
3	2.0 g ,,	13.0	0.065	6.1
4	2.0 g NaBr	1.0	0.033	3.2
5	2.0 g ,,	2.0	0.047	4.5
6	2.0 g ,,	6.0	0.072	6.7
7	2.0 g ,,	10.0	0.076	7.1
8	2.0 g ,,	13.0	0.087	8.0
9	2.0 g NaJ	1.0	0.157	13.6
10	2.0 g ,,	2.0	0.320	24.2
11	2.0 g ,,	6.0	1.06	51.5
12	2.0 g ,,	10.0	1.42	58.7
13	2.0 g ,,	13.0	1.47	59.5

Literatur S. 415

TABELLE VI

VERTEILUNG VON KF-, KCl-, KBr- UND KJ-POLYJODIDEN ZWISCHEN WÄSSRIGEN LÖSUNGEN UND NITROMETHAN IN ABHÄNGIGKEIT VON DER J_2-KONZENTRATION. RAUMTEMPERATUR

Nr	*Wässrige Phase*		*α*	*P%*
	g K-Verbindung pro 100 ml	*g J_2 pro 100 ml*		
1	2.0 g KF	2.0	0.041	3.9
2	2.0 g ,,	10.0	0.11	9.9
3	2.0 g ,,	13.0	0.096	8.8
4	2.0 g KCl	1.0	0.009	0.9
5	2.0 g ,,	2.0	0.022	2.2
6	2.0 g ,,	6.0	0.028	2.7
7	2.0 g ,,	10.0	0.040	3.8
8	2.0 g ,,	13.0	0.039	3.8
9	2.0 g KBr	1.0	0.091	8.3
10	2.0 g ,,	2.0	0.162	14.0
11	2.0 g ,,	6.0	0.326	24.6
12	2.0 g ,,	10.0	0.392	28.2
13	2.0 g ,,	13.0	0.387	27.9
14	2.0 g KJ	1.0	0.381	27.6
15	2.0 g ,,	2.0	0.864	46.4
16	2.0 g ,,	6.0	4.71	82.5
17	2.0 g ,,	10.0	8.82	89.8
18	2.0 g ,,	13.0	11.2	91.8

TABELLE VII

VERTEILUNG VON RbF-, RbCl-, RbBr- UND RbJ-POLYJODIDEN ZWISCHEN WÄSSRIGEN LÖSUNGEN UND NITROMETHAN IN ABHÄNGIGKEIT VON DER J_2-KONZENTRATION. RAUMTEMPERATUR

Nr	*Wässrige Phase*		*α*	*P%*
	g Rb-Verbindung pro 100 ml	*g J_2 pro 100 ml*		
1	2.0 g RbF	2.0	0.062	5.8
2	2.0 g ,,	10.0	0.065	6.1
3	2.0 g ,,	13.0	0.090	8.3
4	2.0 g RbCl	1.0	0.028	2.7
5	2.0 g ,,	2.0	0.042	4.0
6	2.0 g ,,	10.0	0.047	4.5
7	2.0 g ,,	13.0	0.050	4.8
8	2.0 g ,,	20.0	0.051	4.9
9	2.0 g RbBr	1.0	0.189	15.9
10	2.0 g ,,	2.0	0.336	25.2
11	2.0 g ,,	6.0	0.737	42.4
12	2.0 g ,,	10.0	0.797	44.4
13	2.0 g ,,	13.0	0.806	44.6
14	2.0 g ,,	20.0	0.815	44.9
15	2.0 g RbJ	0.4	0.225	18.4
16	2.0 g ,,	1.0	0.605	37.7
17	2.0 g ,,	2.0	1.18	54.1
18	2.0 g ,,	6.0	7.29	87.9
19	2.0 g ,,	10.0	18.3	94.8
20	2.0 g ,,	13.0	19.1	95.0

Literatur S. 415

TABELLE VIII

VERTEILUNG VON CsF-, CsCl-, CsBr- UND CsJ-POLYJODIDEN ZWISCHEN WÄSSRIGEN LÖSUNGEN UND NITROMETHAN IN ABHÄNGIGKEIT VON DER J_2-KONZENTRATION. RAUMTEMPERATUR

Nr	*Wässrige Phase*		*α*	*P%*
	g Cs-Verbindung pro 100 ml	*g J_2 pro 100 ml*		
1	2.0 g CsF	1.0	0.041	4.0
2	2.0 g ,,	2.0	0.081	7.5
3	2.0 g ,,	6.0	0.232	18.8
4	2.0 g ,,	10.0	0.263	20.8
5	2.0 g ,,	13.0	0.259	20.6
6	2.0 g CsCl	1.0	0.086	7.9
7	2.0 g ,,	2.0	0.102	9.3
8	2.0 g ,,	6.0	0.119	10.6
9	2.0 g ,,	10.0	0.135	11.9
10	2.0 g ,,	13.0	0.146	12.7
11	2.0 g ,,	20.0	0.147	12.8
12	2.0 g CsBr	1.0	0.290	22.5
13	2.0 g ,,	2.0	0.559	35.9
14	2.0 g ,,	6.0	1.35	57.4
15	2.0 g ,,	10.0	1.45	59.2
16	2.0 g ,,	13.0	1.47	59.5
17	2.0 g ,,	20.0	1.61	61.7
18	2.0 g CsJ	1.0	1.36	57.6
19	2.0 g ,,	2.0	3.44	77.5
20	2.0 g ,,	6.0	26.9	96.4
21	2.0 g ,,	10.0	67.9	98.6
22	2.0 g ,,	13.0	77.7	98.7
23	2.0 g ,,	20.0	99.2	99.0

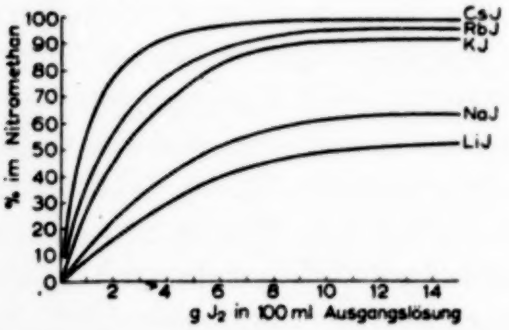

Fig. 2. Verteilung von LiJ-, NaJ-, KJ-, RbJ- und CsJ-Polyjodiden zwischen wässrigen Lösungen und Nitromethan.

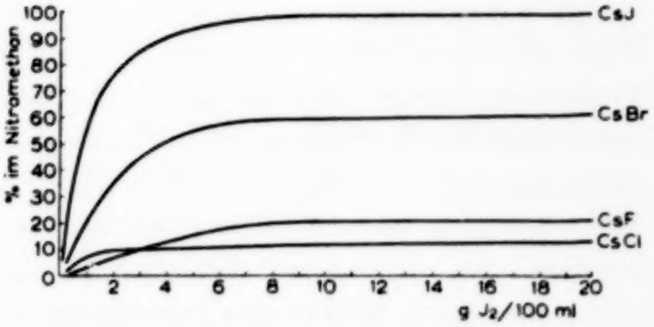

Fig. 3. Verteilung von CsJ-, CsBr-, CsCl- und CsF-Polyjodiden zwischen wässrigen Lösungen und Nitromethan.

TRENNFAKTOREN

Wie schon die verhältnismässig geringen Unterschiede der Verteilungskurven in Abb. 2 zeigen, sind gute Trennungen der Jodide bei Verwendung von Nitromethan nicht zu erwarten, und auch die Polyjodide der anderen Halogenide verhalten sich nicht wesentlich günstiger. Die eigenartige Abhängigkeit der Verteilungskoeffizienten von der Konzentration der ausgeschüttelten Verbindung, die zwar nur für Kaliumjodid näher untersucht wurde, aber bei den anderen Halogeniden ähnlich sein dürfte, lässt ebenfalls diese Systeme als nicht sehr brauchbar erscheinen. Da möglicherweise andere organische Lösungsmittel bessere Ergebnisse bringen konnten, wurden die Trenn-

Literatur S. 415

TABELLE IX

TRENNFAKTOREN BEI VERWENDUNG VERSCHIEDENER ORGANISCHER LÖSUNGSMITTEL

Nr	Lösungsmittel	H_2O-Phase g Jodid	(100 ml) g J_2	α	Trennfaktor β
1	Nitromethan	2.0 g NaJ	2.0	0.285	$\beta_{K,Na} = 3.03$ $\beta_{Rb,K} = 2.25$
2	,,	2.0 g KJ	2.0	0.864	
3	,,	2.0 g RbJ	2.0	1.94	
4	Nitrobenzol	2.0 g NaJ	2.0	0.167	$\beta_{K,Na} = 2.31$ $\beta_{Rb,K} = 1.90$
5	,,	2.0 g KJ	2.0	0.386	
6	,,	2.0 g RbJ	2.0	0.732	
7	Diäthyläther	2.0 g NaJ	2.0	0.141	$\beta_{K,Na} = 1.08$ $\beta_{Rb,K} = 1.30$
8	,,	2.0 g KJ	2.0	0.131	
9	,,	2.0 g RbJ	2.0	0.101	

faktoren für die Verbindungspaare NaJ/KJ und KJ/RbJ unter vergleichbaren Bedingungen mit Nitromethan, Nitrobenzol und Diäthyläther ermittelt (Tab. IX). Die Trennfaktoren wurden dabei rein rechnerisch aus den Verteilungskoeffizienten ermittelt, ohne dass eigentliche Trennungsversuche mit Kalium-Rubidium-Gemischen durchgeführt wurden; sie waren jedoch in keinem Falle befriedigend. Bemerkenswerterweise ist bei Verwendung von Diäthyläther $\alpha_{RbJ} < \alpha_{KJ} < \alpha_{NaJ}$. Da die Trennfaktoren aber auch in diesem System nicht wesentlich von 1 abweichen, wurde auf eine ausführlichere Untersuchung verzichtet.

Ein weiterer Weg zum Erhöhen der Trennungseffekte besteht in der Verwendung organischer Lösungsmittelgemische[9]. Sind zwei Flüssigkeiten bekannt, von denen die eine die zu trennenden Verbindungen gut auszuschütteln, aber schlecht zu trennen vermag, während die andere schlecht ausschüttelt, aber gut trennt, so sind unter Umständen Mischungen zu erwarten, die beide günstigen Eigenschaften in sich vereinigen. Zum Nachweis dieser Möglichkeit wurde das bei der Verteilung gut wirksame Nitromethan mit steigenden Mengen verschiedener anderer organischer Lösungsmittel versetzt und die Verteilung von Kaliumjodid-Polyjodid und Rubidiumjodid-Polyjodid zwischen H_2O-Lösungen und derartigen Gemischen untersucht. Die Zusammensetzung der wässrigen Phasen blieb konstant (10.0 g J_2 und 2.0 g KJ bzw. RbJ in 100 ml); es wurden nur Lösungen mit jeweils einem Alkalimetallpolyjodid untersucht, also wiederum keine wirklichen Trennungsversuche durchgeführt. Die Ergebnisse (Tab. X) zeigen, dass je nach Lösungsmittelpaar verschiedene Effekte auftreten können:

a) Zumischung von Chloroform zum Nitromethan wirkt sich auf KJ- und RbJ-Polyjodid gleichartig aus. Eine wesentliche Verbesserung der Trennfaktoren tritt bei keinem Mischungsverhältnis ein (vgl. Abb. 4).

b) Zumischung von Chlorbenzol bewirkt zunächst ein gleichmässiges Absinken der prozentualen Verteilung beider Verbindungen. Bei grösseren Zusätzen verschlechtert sich jedoch die Verteilung des RbJ-Polyjodids stärker, während die des KJ-Polyjodids ziemlich gleichmässig dem Endwert für reines Chlorbenzol zustrebt (Abb. 5). Es kommt dadurch zu einer Überschneidung der beiden Verteilungskurven, ohne dass jedoch die Trennfaktoren sich wesentlich verbesserten.

Gemische von Nitromethan und Tetrachlorkohlenstoff gaben ähnlich sich schneidende Verteilungskurven.

c) Zumischung von Benzol zum Nitromethan bewirkte ein starkes Absinken der pro-

Literatur S. 415

TABELLE X

TRENNFAKTOREN BEI VERWENDUNG ORGANISCHER LÖSUNGSMITTELGEMISCHE. 2.0 g KJ bzw. RbJ UND 10.0 g J_2 IN 100 ml WÄSSRIGER PHASE

Nr	*Zusammensetzung der organischen Phase (Volumina)*		α_K	α_{Rb}	$\beta_{Rb,K}$
1	100 Nitromethan;	0 Chloroform	8.82	18.3	2.1
2	80 ,, ;	20 ,,	5.85	12.6	2.2
3	60 ,, ;	40 ,,	3.64	9.90	2.7
4	40 ,, ;	60 ,,	1.57	3.78	2.4
5	30 ,, ;	70 ,,	0.727	1.58	2.2
6	20 ,, ;	80 ,,	0.107	0.421	3.9
7	0 ,, ;	100 ,,	ca. 0.005	ca. 0.001	—
8	100 Nitromethan;	0 Chlorbenzol	8.82	18.3	2.1
9	75 ,, ;	25 ,,	5.70	7.66	1.3
10	50 ,, ;	50 ,,	2.52	3.47	1.4
11	35 ,, ;	65 ,,	1.45	1.23	1.2
12	25 ,, ;	75 ,,	0.742	0.421	1.8
13	0 ,, ;	100 ,,	ca. 0.006	ca. 0.001	—
14	100 Nitromethan;	0 Benzol	8.82	18.3	2.1
15	75 ,, ;	25 ,,	0.346	15.3	44
16	50 ,, ;	50 ,,	0.152	7.68	51
17	15 ,, ;	85 ,,	0.021	0.923	44
18	0 ,, ;	100 ,,	0.009	<0.005	—

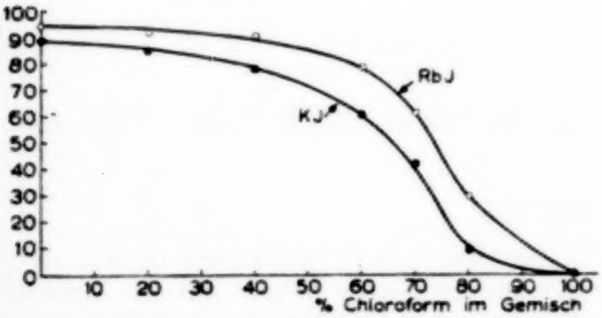

Fig. 4. Verteilung von KJ- und RbJ-Polyjodiden zwischen wässrigen Lösungen und $CH_3NO_2/CHCl_3$-Gemischen.

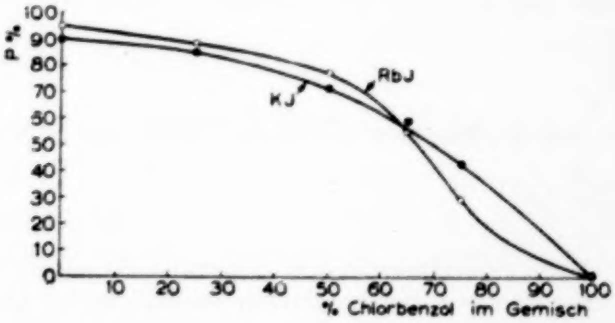

Fig. 5. Verteilung von KJ- und RbJ-Polyjodiden zwischen wässrigen Lösungen und CH_3NO_2/C_6H_5Cl-Gemischen.

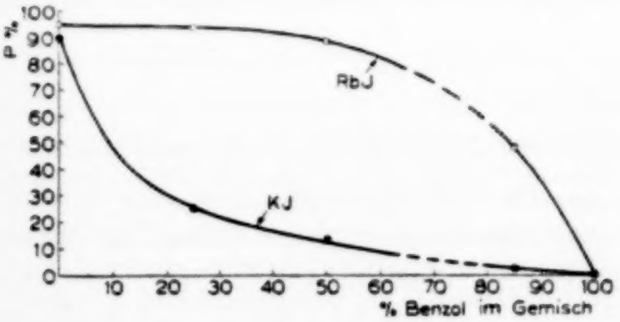

Fig. 6. Verteilung von KJ- und RbJ-Polyjodiden zwischen wässrigen Lösungen und CH_3NO_2/C_6H_6-Gemischen.

zentualen Verteilung des Kalium-Polyjodids schon bei kleinen Benzolgehalten in der organischen Schicht, während die Verteilung des Rubidium-Polyjodids erst bei hohen Benzolkonzentrationen wesentlich abnahm. Infolgedessen erhielt man im Bereich mittlerer Benzolgehalte gute (rechnerisch ermittelte) Trennungseffekte (vgl. Abb. 6). Gemische mit etwa 75% Benzol konnten nicht untersucht werden, da hier die Dichten der wässrigen und der organischen Phase so ähnlich werden, dass eine Entmischung nach dem Schütteln nicht mehr zu erzielen war.

Literatur S. 415

DIE VERTEILUNG WEITERER POLYJODIDE

Die untersuchten Systeme sind nach mehreren Richtungen hin variierbar:

Zunächst wurden einige Verteilungsversuche mit Polyjodiden der Erdalkalibromide durchgeführt; es zeigte sich, dass diese Elemente sich ähnlich wie die Alkalimetalle verhalten, und man wird annehmen dürfen, dass auch in anderen Gruppen des Periodischen Systems analoge Eigenschaften auftreten.

TABELLE XI

VERTEILUNG DER POLYJODIDE EINIGER KALIUMVERBINDUNGEN ZWISCHEN WÄSSRIGEN LÖSUNGEN UND NITROMETHAN. RAUMTEMPERATUR

Nr	*Zusammensetzung der H_2O-Phase 100 ml*		*α*	*P%*
1	2.0 g K_2SO_4	10.0 g J_2	0.006	0.6
2	2.0 g KNO_3	10.0 g J_2	0.006	0.6
3	2.0 g KCNO	10.0 g J_2	0.164	14.1
4	2.0 g KCNS	10.0 g J_2	2.20	68.8

Tab. XI zeigt Versuche, bei denen als Kation ausschliesslich Kalium angewandt wurde, während das Anion wechselte. Sulfat und Nitrat konnten praktisch nicht ausgeschüttelt werden, jedoch gingen die Polyjodide der Kaliumsalze mit den Halogen-ähnlichen Anionen CNO^- und CNS^- deutlich bzw. recht gut in die organische Schicht.

Es besteht schliesslich noch die Möglichkeit, anstelle der Poly*jodide* andere Polyverbindungen, z.B. Polybromide u.a., zu wählen, doch wurde von weiteren Versuchen Abstand genommen.

DANK

Wir danken den Herren D. Rohe und S. Wagener für Mithilfe bei einem Teil der Versuche.

ZUSAMMENFASSUNG

Die Polyjodide der Alkalimetallhalogenide lassen sich aus wässrigen Lösungen mit verschiedenen organischen Lösungsmitteln ausschütteln. Die Verteilungskoeffizienten steigen bei den einzelnen Halogeniden vom Lithium zum Cäsium, bei jedem Alkalimetall vom Chlorid zum Jodid an; die Fluoride ordnen sich — soweit untersucht — zwischen die Chloride und Bromide ein. Die Verteilungskoeffizienten steigen weiterhin mit der Konzentration an freiem Jod. Das Nernst'sche Gesetz gilt im System KJ-J_2-Wasser-Nitromethan nicht. Die Trennfaktoren sind bei Verwendung von Nitromethan, Nitrobenzol und Diäthyläther gering, können jedoch mit Lösungsmittelgemischen verbessert werden.

SUMMARY

Polyiodides of alkalimetal halides can be extracted from aqueous solutions by various organic solvents. The distribution coefficients increase from lithium to cesium halides, and from chlorides to iodides. The fluorides were found to fall between chlorides and bromides in all cases tested. Furthermore the distribution coefficients increase with increasing concentration of free iodine. The Nernst law does not hold in the system KI-I_2-H_2O-nitromethane. The separation factors are small with nitromethane, nitrobenzene and diethyl ether, but can be improved by using mixtures of organic solvents.

RÉSUMÉ

Les polyiodures des halogénures des métaux alcalins peuvent être extraits de leurs solutions aqueuses au moyen de divers solvants organiques. Les coefficients de partage augmentent pour un même halogène du lithium au césium, et de même pour chaque métal alcalin, du chlorure à l'iodure. D'après les travaux déjà effectués dans ce domaine, les fluorures peuvent se classer entre les chlorures et les bromures. Le coefficient de partage augmente également avec la concentration en iode libre. La loi de Nernst ne s'applique pas au système KI-I_2-eau-nitrométhane. Les facteurs de séparation sont faibles lorsqu'on emploie le nitrométhane, le nitrobenzène et l'éther diéthylique; ils peuvent être améliorés en utilisant des mélanges de solvants.

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THE USE OF CACOTHELINE AS AN OXIDATION-REDUCTION INDICATOR BEFORE THE VOLUMETRIC OXIDATION OF IRON

by

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INTRODUCTION

The classical determination of iron, which involves reduction to the ferrous state by an excess of stannous chloride and removal of the latter by addition of mercuric chloride previous to titration, has one outstanding disadvantage. The excess of stannous chloride must be held within rather narrow limits or the determination is ruined either by incomplete reduction or the formation of metallic mercury along with the calomel. TITUS AND SILL[1] suggested that the excess stannous chloride be removed by a preliminary titration using silicomolybdic acid as an indicator. Their procedure gives good results but is rather tedious, it being necessary to remove the silicomolybdic acid by protracted heating. We have found that, under suitable conditions, cacotheline may be used in place of silicomolybdic acid to give equally accurate results in much less time. The method requires no longer than the classical one and is some 25-30 minutes shorter than that of TITUS AND SILL.

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In the titration of the excess stannous chloride, there are three important factors which must be taken into consideration. First, the reaction between stannous and ferric ions is rapid and complete only in hot, strongly acid solution. If a mixture of stannous and ferrous chlorides is titrated potentiometrically with an oxidizing agent at room temperature, a smooth curve is obtained having only one break. Ferric ions, produced by local excesses of oxidant as it is added, are not reduced back to the ferrous state by the stannous chloride present under these conditions, and the mixture behaves as if it contained but a single substance. It is only when the solution is hot that separate potential breaks are obtained for the tin and the iron. Second, the air oxidation of ferrous ions is promoted by high temperatures and acidities. Third, in the visual end-point determination, the indicator must have an oxidation potential such that a very small trace of stannous ion added to a pure ferrous solution will cause a marked change in color, and it must react rapidly and reversibly in hot solution both with stannous tin and ferric iron.

EXPERIMENTAL

A number of indicators, including nile blue, indigo carmine, and methylene blue, with potentials in the proper range were examined and found not to be reduced at a satisfactory rate by stannous chloride. When reduction of the ferric solution was done by means of chromous chloride, indigo carmine was found to be satisfactory indicator but if considerable amounts of iron were present, the green color of the chromic ions formed on reoxidation tended to obscure the color change.

Cacotheline, which has long been used as a sensitive qualitative test for tin[2] was found to be a satisfactory indicator. A trace of stannous ion transforms the canary-yellow compound to a bright violet. The reaction is readily reversible. Since the completion of the present work, others have suggested the use of cacotheline as an indicator in the titration of ferric iron with stannous chloride[3].

Cacotheline is obtainable commercially or may be made from brucine by treatment with nitric acid[2]. The indicator was used as a suspension of 0.5 g in 50 ml of water, 3 to 5 drops being necessary for each titration. The mixture is quite stable. The following procedure was found to give excellent results.

Procedure

A sample containing 2-5 milliequivalents of iron is brought into solution in the usual manner, the volume made about 20-25 ml and 5 ml of concentrated hydrochloric acid added. The mixture is heated almost to boiling and $1N$ stannous chloride added dropwise until the yellow color changes to pale green. A drop or two is added in excess. Keeping the solution hot, 3 drops of cacotheline indicator are added and the mixture rapidly titrated with 0.02-$0.03N$ ceric sulfate until the violet color fades to brown and then changes sharply to a clear yellow. It is advisable to add one or two drops more indicator just before the end-point as there is some desensitization by the oxidant in the hot, strongly acid solution. This ceric sulfate need not, of course, be standardized nor any buret readings taken. By having this solution only one-third to one-fifth as concentrated as the actual standard solution, the accuracy is considerably increased and there is no necessity of splitting drops in the first titration.

Two hundred ml of water, and 6 ml of $18N$ sulfuric acid are next added and the mixture titrated with standard $0.1N$ ceric sulfate, orthophenanthroline ferrous complex being used as the indicator. If diphenylamine sulfonic acid is preferred as the indicator, 5 ml of 85% phosphoric acid is added to the solution before the sulfuric acid. The phosphoric acid lowers the oxidation potential of the ferrous-ferric couple and may cause a reappearance of the violet cacotheline color. This color does not indicate anything wrong, and it disappears during the subsequent titration.

The presence of the cacotheline does not have any effect on the color change of the diphenylamine sulfonic acid. Dichromate may be used satisfactorily for the second titration but not for the first as the end-point is not sharp. This seems to be due partly to preferential oxidation of the indicator. It is also known that chromic ions interfere with the stannous-cacotheline reaction[4].

Results

Aliquot portions of a stock ferric sulfate solution were titrated by this method and also by the accepted mercuric chloride method[5]. After the cacotheline end-point or the addition of mercuric chloride, an amount of standard ceric sulfate slightly less than that equivalent to the iron present was added from a pipet and the titration finished with a microburet, a technique which permits estimation of the titration volume to about 0.002 ml. Some typical data shown in Table I indicate that the two methods give virtually identical results.

TABLE I

ml OF 0.1N $Ce(SO_4)_2$ TO TITRATE 25 ml OF Fe STOCK SOLUTION

	Cacotheline method	*Mercuric chloride method*
	23.68	23.67
	23.69	23.71
	23.69	23.69
	23.68	23.69
	23.68	23.70
Ave.	23.68	23.69

Some titrations were attempted with 0.01N solutions but it was found that the first end-point, as determined using correspondingly more dilute ceric sulfate, was not sufficiently sharp to give accurate results. The double indicator titration yielded results consistently 1% higher than the mercuric chloride method.

The presence of one-fifth as much titanium(IV) as iron was found to have no effect on the results. The presence of one-fifth as much vanadium(IV) or (V) as iron in the original sample made the first end-point a little less sharp and larger amounts caused trouble. As is well known, the titration of iron to a diphenylamine sulfonate end-point is not exact in the presence of vanadium unless the acidity is fairly high. The present procedure gave results about 0.5% high at an iron-to-vanadium ratio of 5 to 1. Addition of an additional 10 ml of concentrated sulfuric acid to the final titration mixture removed this error. Analysis of U.S. National Bureau of Standards *Sibley* iron ore gave a result of 68.62% iron, the average deviation of four determinations being 0.07% iron, in good agreement with the Bureau's certificate value of 68.57%.

A brief study was made of the oxidation-reduction behavior of cacotheline. Although stannous chloride gives the violet color much more readily than any other substance, a number of other reagents will cause the color change to some extent. It has long been known that titanium(III), vanadium(III), rhodium(III), niobium(III) and uranium(III) ions as well as reduced molybdenum and tungsten solutions, copper(I) chloride, and iron(II) salts in the presence of phosphate or fluoride may give similar colors in the qualitative test for tin[4,6,7]. We found also that metallic mercury when shaken with solutions of the indicator in perchloric, sulfuric, and hydrochloric acids gave a transient violet color. When polarographic measurements were made on solutions of cacotheline in $0.1N$ hydrochloric and perchloric acid, two well-defined waves were obtained, with half-wave potentials at $+0.09$ V and -0.23 V (*versus* the saturated calomel electrode). The first wave probably corresponds to the reversible step involving the color change, and the second wave to the irreversible reduction to a colorless substance observed with strong reductants like metallic tin.

ACKNOWLEDGEMENT

The authors wish to express their appreciation to the Graduate School of the University of Minnesota for financial aid.

SUMMARY

Cacotheline may be used as an oxidation-reduction indicator in the removal of stannous tin with ceric sulfate before the titration of ferrous iron.

RÉSUMÉ

La cacothéline peut-être utilisée comme indicateur d'oxydoréduction, lors de l'oxydation de l'étain(II) par le sulfate de cérium(IV), effectuée avant le titrage du fer(II).

ZUSAMMENFASSUNG

Cacothelin kann als Oxydations-Reduktions-Indikator bei der Oxydation von Zinn(II) mit Cer(IV)sulfat, welche der volumetrischen Bestimmung von zweiwertigem Eisen vorangeht, verwendet werden.

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A RAPID ROUTINE METHOD FOR THE DETERMINATION OF ZINC IN WOOD PRESERVATIVES

by

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The ferrocyanide titration of zinc using *o*-dianisidine is a rapid and accurate method for the determination of zinc. However, copper and trivalent chromium must be absent. In the method[1] recently described these interferences were eliminated by the removal of copper and chromium before the titration. It seemed however desirable to find a method of removal of the zinc from the solution free from these metals and so reduce the time required for the analysis. It has been found that zinc can be precipitated as phosphate if the copper is masked with glycine and the chromium is present as chromate and this is achieved on the basis of the following method.

Reagents

1% Glycine.
10% Disodium phosphate neutralized to pH 7 using bromothymol blue.
Ammonium hydroxide *N*.
Sulphuric acid 1 : 1.
Ammonium sulphate A.R.
Standard potassium ferrocyanide 21 g/litre.
o-Dianisidine 0.1%. 0.1 g of the indicator is dissolved in 1 ml of conc. H_2SO_4 and diluted to 100 ml with distilled water.
Bromothymol blue 0.1%.

Procedure

1. To the sample containing about 20 mg of zinc in 30-40 ml add 10 ml of glycine solution and neutralize with ammonium hydroxide to pH 6.5-7.5 using bromothymol blue as indicator.
2. Add 5 ml of phosphate and boil gently until the precipitate coagulates.
3. Filter through a 1 F paper and wash with hot wash liquid containing 1% glycine and 1% phosphate at pH 7.
4. Return the filter paper to the original beaker, add 3 ml of 1 : 1 sulphuric acid, 2 g of ammonium sulphate and 30 ml of distilled water.
5. Heat to boiling, remove the source of heat and titrate with standard ferrocyanide following the method[1] previously described.

DISCUSSION

It became apparent early in the investigation that although copper did not precipitate in the above procedure, complete precipitation of zinc was not obtained. Analysis of pure zinc solutions showed that this was due to the solubility of the zinc phosphate. The glycine appeared to have little effect. If the amount of zinc taken was greater than

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[1] W. J. WILSON, *Anal. Chim. Acta*, 15 (1956) 508.

15 mg/50 ml reproducible results were obtained. Thus by standardizing the ferrocyanide against known amounts of zinc taken through the procedure reliable results could be obtained. These solubility effects are illustrated in Table 1.

TABLE I

Zn taken *mg*	*Direct titration* *mg*	*Titration after ppt with PO_4^{-3}; no glycine* *mg*	*Ppt with PO_4^{-3} + glycine* *mg*
(a) 5.00	5.03	4.66	4.63
(b) 10.00	10.00	9.78	9.68
(c) 15.00	14.95	14.65	14.75
(d) 20.00	20.00	19.69	19.80

The order of addition of the reagents is important. Addition of the phosphate before neutralization results in some contamination of the precipitate with copper. For the same reason the phosphate must be added to the cold solution. During the neutralization zinc precipitates as hydroxide or arsenate but it is found experimentally that the filtering characteristics of the precipitate are much improved by the addition of phosphate and boiling.

Results obtained by the method are in good agreement with those obtained by the slower method and demonstrate the value of the method as a rapid routine procedure.

ACKNOWLEDGEMENTS

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SUMMARY

A method is described for the rapid routine determination of zinc in wood preservatives. Zinc is separated from interfering chromate and copper by precipitation as phosphate from neutral solution in the presence of glycine followed by titration with ferrocyanide. This method is suitable for zinc concentrations in the range 0.3-0.6 mg Zn/ml.

RÉSUMÉ

Une méthode est décrite pour le dosage en série du zinc dans des antiseptiques du bois. Le zinc est séparé du chromate et du cuivre (qui gênent le dosage) par précipitation comme phosphate, en solution neutre, en présence de glycine; on effectue ensuite un titrage au moyen de ferrocyanure. Cette méthode permet de doser des teneurs en zinc allant de 0.3 à 0.6 mg/ml.

ZUSAMMENFASSUNG

Eine Methode für schnelle Routine-Bestimmungen von Zink in Holzimprägnierungslösungen wird beschrieben. Das Zink wird von Chromat und Kupfer durch Fällung als Phosphat aus neutraler Lösung in Gegenwart von Glycin getrennt und dann mit Ferrocyanid titriert. Die Anwendung dieser Methode ist nur für Zink-Konzentrationen von 0.3 bis 0.6 mg/ml erfolgreich.

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THE SEPARATION OF BERYLLIUM FROM IRON, ALUMINIUM AND TITANIUM BY ION EXCHANGE, AND ITS APPLICATION TO THE ANALYSIS OF BERYL

by

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Ion exchange methods have been applied for the isolation and estimation of beryllium from biological samples[1] and alloys[2] but not for estimation of beryllium in minerals and ores.

The beryllium complex of ethylene diamine tetraacetic acid (EDTA) at a pH of about 4, is much weaker than the corresponding complexes of iron and aluminium. It was, therefore, considered possible to effect a complete separation of beryllium from iron and aluminium on a cation exchange resin, making use of this difference in stabilities of the EDTA complexes, especially where beryllium has to be separated from large amounts of aluminium as in the analysis of beryls.

EDTA has been used as a complexing agent in the analysis of beryllium minerals in the following three methods: (i) the precipitation of beryllium as beryllium ammonium phosphate, after complexing interfering elements with EDTA, and its ignition to the pyrophosphate[3]; (ii) the precipitation of beryllium as beryllium ammonium phosphate in the presence of EDTA, and its volumetric estimation[4]; (iii) the precipitation of beryllium hydroxide, using EDTA as complexing agent for the interfering elements, and its ignition to the oxide[5]. In the last method phosphate interferes because it accompanies the hydroxide precipitate. Moreover, because the titanium complex of EDTA is weak, this element is also liable to contaminate the beryllium precipitate.

In the present method interference from titanium as well as phosphate has been eliminated.

EXPERIMENTAL

Apparatus and reagents

Ion exchange column: The common type of ion exchange column was used. The main column consisted of a pyrex glass tube 1.8 cm in diameter and 20 cm long. A 125-ml separating funnel was fitted over the tube for holding the solutions.

Ion exchange resin: Amberlite IR-120, 0.4-0.6 mm, filled to a height of 12 cm in the column.

Reagents: All reagents used were of C.P. grade.

General procedure

To the solution containing beryllium, aluminium, etc., a solution of EDTA (disodium salt) was added and the required pH was adjusted. This solution was then passed through the column containing the resin in the sodium form. After passing the entire solution, the column was washed with 0.5% EDTA solution and later with distilled water. The adsorbed beryllium was then recovered by eluting with $3N$ hydrochloric acid and estimated gravimetrically after precipitation as hydroxide.

The sodium form of the resin was used because the hydrogen form disturbed the pH of the solution and had a tendency to cause precipitation of the EDTA owing to the low solubility of the acid.

Rate of flow

The rate of flow during the sorption step was first studied and the results are shown in Table I. It is seen that with a flow rate of 10 ml/min and above, the beryllium is not quantitatively held up by the resin column. In order to have a wide margin of safety a flow rate of about 5 to 6 ml/min (approx. 2 ml sq.cm^{-1}min^{-1}) was maintained for all further experiments. The same rate was maintained for the washing and elution steps also.

TABLE I

RATE OF FLOW

Rate ml/min	*BeO taken* mg	*BeO found* mg
5	51.0	51.2
10	51.0	50.4
15	51.0	40.6

Elution with acid

In order to establish the volume of $3N$ hydrochloric acid necessary for completely eluting out the beryllium, the column was eluted with different volumes of the acid after the sorption and washing stage. After passing the acid, the column was rinsed with 100 ml of distilled water in each case. 150 ml of the acid were considered necessary for this step, although the results (Table II) indicate that all beryllium is eluted by 100 ml of the acid.

TABLE II

ELUTION

3N HCl ml	*BeO taken* mg	*BeO found* mg
50	52.5	44.4
100	52.5	52.7
150	52.5	52.6

Effect of pH

Since the stabilities of the EDTA complexes vary with pH, it was to be expected that change of pH would have considerable effect on the separation of beryllium from aluminium and iron. It is seen from the results in Table III that below a pH of 2 a considerable quantity of alumina accompanies the BeO precipitate owing to the comparative weakness of the aluminium complex at this pH. Between pH 2.5 and 4.5 the separation was quantitative. The BeO precipitate was in each case tested with oxine for its purity. A pH of about 3.5 was considered most suitable as the stabilities of the iron and aluminium complexes are highest at about this pH. Moreover beryllium starts precipitating as phosphate at a pH of about four in the event of phosphate being present.

Separation from common ions

The ion exchange separation of beryllium was undertaken with a view to adopting it for the estimation of BeO in beryl. The minerals likely to be associated with beryl are quartz, felspar, apatite and mica. In addition to cations present in these minerals it was

TABLE III

EFFECT OF PH

pH	*BeO taken* *mg*	*Total R_2O_3 found* *mg*
1.5	64.5	98.1
2.0	52.5	58.7
2.5	64.5	64.3*
3.5	56.5	56.2*
4.5	64.4	64.5*

(Approximately 6-8 mg Fe_2O_3 and 70-80 mg Al_2O_3 were taken along with the beryllium).

*Precipitate tested with oxine and found free from Fe and Al.

considered necessary to pay special attention to small amounts of titanium which is likely to be present, particularly because it also forms a weak complex with EDTA. Results of separation of common cations in artificial mixtures are given in Table IV. Whenever titanium was added it was complexed by means of hydrogen peroxide before the sorption step. The titanium was found to pass into the effluent quantitatively as an anion. According to SAMUELSON[6], phosphoric acid is adsorbed to a certain extent by cation exchange resins, and the adsorbed acid can be quantitatively removed by using a sufficiency of water during the washing process. Whenever phosphate was added, therefore, a larger amount of water was used for washing, and this was found to eliminate phosphate quantitatively. The BeO precipitate obtained finally was tested for the respective impurities added in each case. These were found to be either completely absent or present in such minute traces as not to affect the results. Apart from the purity of the beryllium separated, Table IV shows a complete separation from Fe, Al, Ti, Ca and P_2O_5.

TABLE IV

ANALYSIS OF SYNTHETIC MIXTURES

BeO taken mg	*Al_2O_3 added mg*	*Fe_2O_3 added mg*	*TiO_2 added mg*	*CaO added mg*	*P_2O_5 added mg*	*BeO found mg*	*Difference mg*
66.3	87.5	8.0	4.1	—	—	66.9	+ 0.6
52.5	75.0	—	—	—	—	52.5	nil
10.5	75.0	—	—	—	—	10.7	+ 0.2
78.8	75.0	—	—	—	—	78.7	— 0.1
52.5	—	16.0	10.0	—	—	52.6	+ 0.1
52.5	—	16.0	—	56.0	50.0	52.7	+ 0.2
52.5	50.0	16.0	—	28.0	25.0	52.8	+ 0.3

Analysis of beryl

The following procedure was used for the analysis of beryls: 0.5 g of the ground sample was weighed into a platinum crucible and fused for about 10 min with 2 g of sodium fluoride. After cooling, 5 ml of 1 : 1 H_2SO_4 were added and the covered crucible heated slowly on the sand bath. After the evolution of fluosilicic and hydrofluoric acids had ceased, the crucible was opened and heated more strongly till the evolution of SO_3 fumes started. The crucible was then heated over a direct flame until a clear melt was obtained. After cooling the contents of the crucible were extracted in 150-200 ml of water in a 600 ml beaker, when a clear solution was obtained. To this solution were added 20 ml of a 10% solution of the disodium salt of EDTA and the volume made to approximately 400 ml. The pH was adjusted to 3.5 by means of a 10% solution of sodium hydroxide, and 1 ml of hydrogen peroxide (100 vols.) was added when the solution was ready for the ion exchange column. (In case titanium was known to be absent in the sample, the addition of peroxide was not made.)

The resin was first converted to the sodium form by passing 100 ml of a 10% solution of sodium chloride and washing with about 150 ml of distilled water. The solution to be analysed was then passed through the column at a rate of about 5 to 6 ml per minute. The column was next washed with 150 ml of a 0.5% EDTA solution of pH 3.5, followed by 200 ml of distilled water. (When phosphate was known to be absent only 100 ml of water was used for this step.)

The adsorbed beryllium was recovered by eluting with 150 ml of 3*N* hydrochloric acid followed by 100 ml of water, and estimated gravimetrically by igniting to BeO after double precipitation as hydroxide with ammonia with usual precautions.

Table V shows the results of analysis of a number of beryl samples analysed by the present method as compared with analyses by the standard gravimetric method[7], and the volumetric method recommended by DAS AND ATHAVALE[4]. It is seen that the results compare well. Experiment 9 in the table is with a mixture of 0.25 g of a previously analysed beryl with 0.25 g of calcium phosphate. The mixture after fusion with sodium fluoride and subsequent fuming with sulphuric acid did not give a clear solution owing to the low solubility of calcium sulphate. This was dissolved by the addition of about 5 ml conc. HCl, and the third group elements precipitated by ammonia. The precipitate was redissolved in dil. HCl containing 5 ml of the concentrated acid, and the solution used for the analysis.

TABLE V

ANALYSIS OF BERYL SAMPLES

Serial no.	*% BeO*		
	Gravimetric	*Volumetric*	*Ion exchange*
1	12.88	12.88	12.90
2	11.80	12.03	11.76
3	12.00	11.98	11.80
4	—	8.80	8.90
5	—	12.43	12.54
6	11.30	11.19	11.24
7	10.38	10.50	10.58
8	—	1.90	1.98
9	6.44	6.44	6.45

Experiment 8 shows that the method also works in cases where the BeO content of the sample is very low.

Further work is in progress to adapt this method for the recovery and analysis of beryllium in materials containing microgram quantities of the element.

SUMMARY

A new ion exchange method is proposed for the separation of Be from Al, Fe, Ti, Ca and phosphate, by preferentially adsorbing it on cation exchange resin Amberlite IR-120, after complexing the other ions with EDTA and H_2O_2. The successful application of the method to the analysis of beryls is demonstrated.

RÉSUMÉ

Une nouvelle méthode par échange d'ions est proposée pour la séparation de Be d'avec Al, Fe, Ti, Ca et phosphate, en adsorbant de préférence sur la résine Amberlite IR-120, pour échange de cations; on complexe au préalable les autres ions avec EDTA et H_2O_2. Cette méthode a été appliquée avec succès à l'analyse des béryls.

ZUSAMMENFASSUNG

Eine neue Methode zur Trennung des Be von Al, Fe, Ti, Ca und Phosphat durch dessen bevorzugte Adsorption an dem Kationenaustauscherharz Amberlite IR-120, nach Komplexierung der anderen Ionen mit EDTA und H_2O_2 wird beschrieben. Die erfolgreiche Anwendung der Methode auf die Analyse des Berylls wird bewiesen.

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THE DETERMINATION OF NITRATE AND CHLORIDE IN SODIUM HYDROXIDE SOLUTIONS BY MEANS OF CATION EXCHANGERS, IN THE MANUFACTURING CONTROL OF ALKALINE BATTERIES

by

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Alkaline batteries are of two types: 1) The Edison cell and 2) the nickel-cadmium cell. This latter type can be divided further into the older Jungner type and the impregnated sintered-plate type.

The sintered-plate nickel-cadmium cell differs considerably in the technical performance from the other two types. The plates, both the positive and the negative, consist of a highly porous structure of nickel, impregnated with nickel hydroxide and cadmium hydroxide respectively, which form higher nickel oxides and cadmium metal respectively during charging. The impregnation of the plates is accomplished in solutions of nickel and cadmium salts, preferably nitrates but also chlorides. When the porous nickel plates have been filled with the salt solution, they are immersed in a strong sodium hydroxide solution, when the corresponding hydroxides precipitate in the pores of the plates. The plates are then rinsed in water and dried at 80°C. This cycle of impregnation is repeated 3 or 4 times, when the plates are ready for charging.

As the sintered nickel plates have a very high porosity (usually about 80%) every plate adsorbs a large volume of the impregnating salt solution which means that the sodium hydroxide solution is rapidly neutralized when the filled plates are immersed in it, and more sodium hydroxide must be added. Through this the nitrate and chloride concentrations in the hydroxide solution increase and as these ions are injurious to the alkaline battery it is very important that their concentration does not become too high, in which case the risk of occlusion in the precipitated metal hydroxide is large. In order to determine these ions in the sodium hydroxide solution the following simple, rapid and accurate ion-exchange method has been developed. The solution is passed through a cation exchanger in the hydrogen form and the effluent is titrated with 0.1*N* sodium hydroxide in the presence of methyl orange as indicator.

APPARATUS

The cation exchanger used was of sulfonic acid type, Amberlite IR-120, with a particle size of 0.15-0.30 mm in air-dry condition. The columns were of ordinary type. The height and diameter of the resin layer were respectively 150 mm and 10 mm in the experiments described.

The ion exchanger was transformed into the hydrogen form by passing 150 ml of 3*N* hydrochloric acid through the column and subsequently washing with water until the effluent gave a neutral reaction.

EXPERIMENTAL

The salt solutions and sodium hydroxide solution used for impregnating the sintered plates of the cell are rather concentrated. In experiments with synthetic solutions a 10*N* sodium hydroxide solution was used, to which known volumes of 1*N* nitric and hydrochloric acid respectively were added. These solutions were diluted ten times and ten ml of these diluted solutions were passed through the cation exchange layer. After washing with 50 ml distilled water the combined effluent and wash water were titrated with 0.1*N* sodium hydroxide with methyl orange as indicator. The results of these experiments are given in Table I. The method is very accurate, the maximum relative error being 0.5%.

TABLE I

NO_3 *added* *g/l*	NO_3 *found* *g/l*	*Relative error* %	*Cl* *added* *g/l*	*Cl* *found* *g/l*	*Relative error* %
31.20	31.32	+0.38	29.28	29.25	—0.11
46.80	46.95	+0.32	43.92	44.11	+0.43
62.40	62.71	+0.50	58.56	58.85	+0.49
78.00	77.97	—0.04	73.20	73.74	+0.44
94.60	94.13	—0.50	87.84	88.20	+0.41

The method outlined above has been used for the manufacturing control of the impregnating solutions. The sintered nickel plates of the battery had been impregnated with cadmium chloride solutions and the chloride content in the sodium hydroxide solution was determined both by the ion exchange method described here and by titration according to MOHR. The results presented in Table II show good agreement between the two methods.

TABLE II

Cl g/l found according to *ion exchange method*	*Cl g/l found according to* MOHR's *titration*
52.00	51.82
38.57	38.93
66.32	66.35
60.19	60.34
49.11	49.01

DISCUSSION

As is seen above the method outlined is simple and accurate when determining the chloride or nitrate content in the impregnating sodium hydroxide solutions. Obviously, if impurities, consisting of foreign salts, are present in the solution, these salts are also determined, because they react with the ion exchanger according to the formula (MeA denotes the foreign salt):

$$\mathrm{MeA} + \mathrm{R\text{-}SO_3H} \rightarrow \mathrm{R\text{-}SO_3Me} + \mathrm{HA}$$

the liberated acid HA being titrated in the final titration. The impregnated solutions used, however, are prepared from very pure chemicals. The salts determined by the ion exchange method in the impregnating hydroxide solutions can therefore be considered to have been formed only by the reaction of the nickel or cadmium salt with sodium hydroxide. The results of the ion exchange method may also be misleading because of the formation of sodium carbonate in the hydroxide solutions. If the carbonic acid, formed on passing through the resin layer, is not boiled out, the titration result will be too high. However, as the impregnation is performed in covered tanks and the solutions are discarded within a short time, when used in the production of impregnated plates, the error owing to this will be small, which is also seen from Table II. The use of methyl orange is important in this connection.

As the titrimetric determination of chloride, *e.g.* according to MOHR or VOLHARD, is simple and accurate, the ion exchange method outlined in this paper is not so important in this case. The nitrate, however, is very difficult to determine quantitatively; in most cases it is reduced to ammonia, which is distilled and absorbed in an acid of known normality, which is titrated afterwards. The method described here is therefore very convenient when nitrate is present in the hydroxide solution, as it is much more simple and accurate than other methods, which is the more important as nitrate solutions are by far the most common for the impregnation of sintered nickel plates.

SUMMARY

The most important types of alkaline batteries are described. A method for the determination of chloride and nitrate ions in sodium hydroxide solutions has been developed. The analysis is performed in the following manner: the solution is passed through a layer of a cation exchanger in the hydrogen form, whereby the sodium hydroxide is neutralized. The liberated hydrochloric and nitric acids respectively are determined through titration. This method has been used for the manufacturing control of nickel-cadmium batteries.

RÉSUMÉ

Les modèles de batteries alcalines les plus importantes sont décrites. Une méthode est proposée pour le dosage des anions chlorhydrique et nitrique dans des solutions d'hydroxyde de sodium. L'analyse s'effectue de la manière suivante: la solution est passée à travers un échangeur de cation (forme hydrogène): l'hydroxyde de sodium est ainsi neutralisé et les acides chlorhydrique et nitrique libérés sont titrés par un hydroxyde alcalin. Ce procédé a été utilisé pour le contrôle de fabrication des batteries nickel-cadmium.

ZUSAMMENFASSUNG

Die wichtigsten Typen von alkalischen Batterien werden beschrieben. Eine Methode zur Bestimmung der Chlorid- und Nitrat-Ionen in Natriumhydroxyd-Lösungen wurde entwickelt. Die Analyse wird folgendermassen ausgeführt: Die Lösung wird durch eine Lage Kationenaustauscher (in der Wasserstofform) geführt, wobei das Natriumhydroxyd neutralisiert wird. Die in Freiheit gesetzte Salz- und Salpetersäure werden durch Titration bestimmt. Diese Methode wurde bei der Fabrikationskontrolle von Nickel-Cadmium-Batterien angewendet.

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SEPARATION OF CAFFEINE FROM ANTIPYRINE BY MEANS OF CATION EXCHANGER IN THE FERRIC IRON FORM

by

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In an earlier paper[1] it was shown that β-diketones which form stable iron complexes can be taken up by a cation exchanger in the ferric iron form. A quantitative method was devised for their separation from monoketones and β-diketones. In the present investigation it was found, that a resin in the ferric iron form can be utilized for the separation of caffeine and antipyrine: antipyrine is completely retained in a column filled with ferric iron resin, whereas caffeine under suitable conditions passes through.

The usual methods for the estimation of caffeine in the presence of antipyrine are laborious and more or less inaccurate[2]. The chromatographic method proposed by VALENTIN AND BRODERSEN-KIRCHÜBEL[3] and modified by BISTER AND WOLFF[2] seems to be the most convenient. However, the ion exchange method presented in this paper is simpler and the results obtained are more accurate. Furthermore, the ion exchange resin is capable of taking up much larger amounts of antipyrine than the chromatographic adsorbent. Finally, no organic solvents are required, as the separation is carried out in aqueous solution.

EXPERIMENTAL

Ion exchange columns of standard type[4] with resin bed dimensions of 9 × 160 mm were used. The cation exchange resin, Dowex 50, was ground in the air-dried state and screened to obtain a particle size of 0.15 to 0.30 mm. After the usual treatment[4], the resin was converted into the ferric iron form with about 50 ml of 10% ferric chloride and finally washed with water until the effluent was free from iron. The washing was continued until the absorbance of the effluent was less than 0.05 at 271 mμ. In the experiments carried out at elevated temperature the columns were placed in a water thermostat adjusted to 50 ± 0.5°C and to 70 ± 0.5°C, respectively. Since the complex formation takes place rather slowly, the flow-rate was regulated with the stopcock to about 1 ml/min both during the sorption step and at the beginning of the washing with the first 25-50 ml. The flow-rate was then increased to about 4 ml/min.

Caffeine and antipyrine were determined spectrophotometrically in the ultraviolet region, the absorption maxima being 271 mμ and 240 mμ, respectively. A Unicam S.P. 500 Spectrophotometer fitted with matched 1-cm absorption cells was used for the measurements.

RESULTS AND DISCUSSION

The displacement of caffeine and the sorption of antipyrine were first studied in order to determine the most suitable conditions for their separation.

It was found that on passing an aqueous solution of caffeine through the column, a

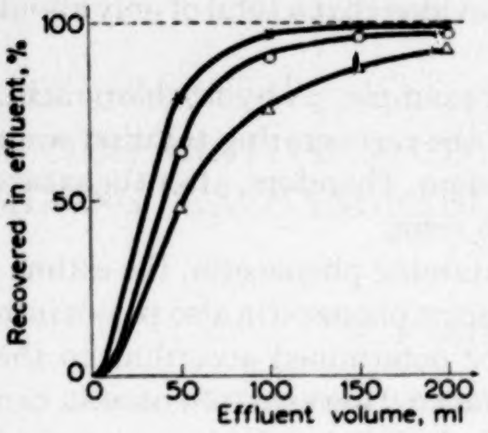

Fig. 1. Washing step of caffeine
Δ — Δ Water at 25°C
o — o Water at 50°C
x — x Water at 70°C

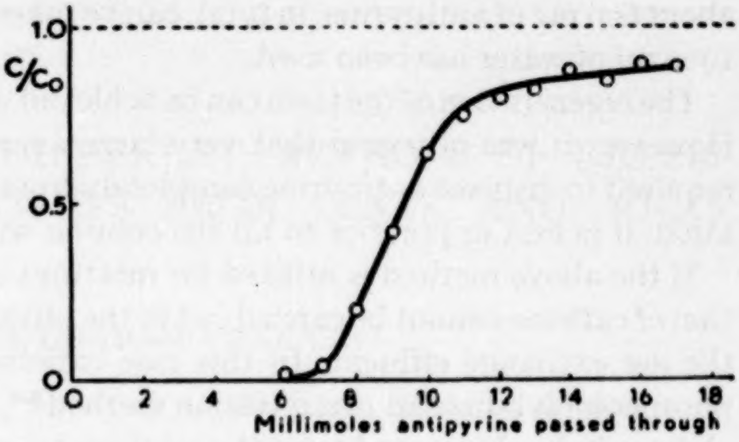

Fig. 2. Break-through curve of antipyrine (0.02 mol/l in water at 70°C). Total capacity of the column 7.47 mmol Fe^{+3}
C_0 = Concentration of the influent
C = Concentration of the effluent

proportion of the caffeine is retained by the resin. As can be seen from Fig. 1, relatively large amounts of water are required to wash caffeine quantitatively from the column at room temperature. However, at elevated temperature the displacement proceeds more readily. Consequently, at 70°C, 99.9% of the caffeine is recovered with 200 ml of water. The difficult displacement of caffeine apparently depends upon physical adsorption, and hence naturally decreases with rise of temperature.

The break-through curve of antipyrine at 70°C is presented in Fig. 2. As can be seen, about 4 mmoles (752 mg) can be passed through the column before antipyrine appears in the effluent. When the break-through point has been reached, the concentration of antipyrine in the effluent first increases relatively rapidly. In the end, however, the break-through curve rises very slowly and when 18 mmoles of antipyrine have passed through the column the concentration of the effluent is about 90% of that of the influent ($C/C_0 \sim 0.9$).

On the basis of the above results a quantitative separation of caffeine from antipyrine was carried out as follows: The mixture dissolved in about 25 ml of water, was passed through the column at 70°C. Caffeine was washed out with water to obtain an effluent volume of 250 ml and estimated in the ultraviolet. As can be seen from Table I, a high degree of accuracy was obtained even in the presence of relatively large amounts of antipyrine.

TABLE I

DETERMINATION OF CAFFEINE IN THE PRESENCE OF ANTIPYRINE

Antipyrine added mg	*Caffeine added* mg	*Caffeine found* mg	*Error* %
100	100	101.9	+1.9
250	100	99.8	—0.2
250	50	50.9	+1.8
100	25	25.1	+0.4
250	25	24.8	—0.8

It must be pointed out that when water is passed through the resin bed, antipyrine gradually moves downwards in the column. Therefore, the quantity of antipyrine which can be taken up also depends upon the amount of water used. With a safety margin, about 600 mg of antipyrine, in total, can be taken up, provided that a total of only about 1000 ml of water has been used.

The regeneration of the resin can be achieved with, for example, 3*N* hydrochloric acid. However, it was observed that very large amounts of the regenerating solution were required to displace antipyrine completely from the column. Therefore, after the saturation, it is best in practice to fill the column with fresh resin.

If the above method is utilized for mixtures also containing phenacetin, the estimation of caffeine cannot be carried out in the ultraviolet, since phenacetin also passes into the ion exchange effluent. In this case caffeine can be determined according to the phosphomolybdic acid precipitation method[5,6], for instance. However, phenacetin can also easily be eliminated from the mixture by acid hydrolysis, whereby it is converted into *p*-phenetidin. When the acidic solution is extracted with chloroform, only caffeine and antipyrine are dissolved in the chloroform phase. After the solvent has been evaporated, the residue is dissolved in water and passed through the column. Consequently, the estimation of caffeine can be carried out in the ultraviolet.

SUMMARY

The ion exchange separation method presented in this paper is based upon the ability of antipyrine to form complexes with ferric iron. On passing an aqueous solution of caffeine and antipyrine through a cation exchanger in the ferric iron form, antipyrine is quantitatively taken up. Caffeine, however, is completely displaced from the column on washing with water at elevated temperature and determined spectrophotometrically in the ultraviolet region. This procedure has been found to be simpler and more precise than others previously used.

RÉSUMÉ

La méthode proposée est basée sur la propriété de l'antipyrine de former des complexes avec le fer(III). En faisant passer une solution aqueuse de caféine et d'antipyrine à travers une colonne d'échange de cations (sous forme de fer(III)) l'antipyrine est retenue quantitativement sur la colonne. La caféine par contre est complètement entraînée par lavage à l'eau, à chaud; elle peut être dosée ensuite spectrophotométriquement dans l'ultra-violet. Ce procédé est plus simple et plus précis que d'autres déjà utilisés.

ZUSAMMENFASSUNG

Das Vermögen von Antipyrin, Komplexe mit Eisen(III) zu bilden, liegt der mitgeteilten Methode zugrunde. Wenn man eine wässrige Lösung von Koffein und Antipyrin durch einen Kationenaustauscher in Ferriform laufen lässt, wird Antipyrin quantitativ in der Säule zurückgehalten. Koffein lässt sich vollständig mit Wasser bei erhöhter Temperatur aus der Säule verdrängen und spectralphotometrisch im UV-Bereich bestimmen. Das Verfahren ist einfacher und genauer als andere, früher beschriebene Methoden.

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A COMPARATIVE STUDY OF DIFFERENT METHODS OF DETERMINING EXCHANGEABLE CATIONS FROM CLAYS AND MICAS

by

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Accurate determination of the exchangeable cations has been a difficult problem chiefly due to the incomplete replacement of the cations from the cation exchange systems and the solubility effects. Various investigators have proposed different methods from time to time. Some of the methods have been completely abandoned due to their limitations, whereas others are used with some degree of accuracy. HENNEBERG AND STOHMANN[1] were the first to recognize that to demonstrate the stoichiometry of base exchange, it is necessary to distinguish between exchange and pure solubility.

The exchangeable cations in the clays and micas can be replaced by (1) leaching with concentrated salt solutions (*e.g.* NH_4Cl, CH_3COONH_4, NaCl, $BaCl_2$), (2) leaching with dilute acids (*e.g.* 0.04N HCl, 0.5N CH_3COOH), (3) electrodialysis.

Dilute HCl was used in one of GEDROIZ's original methods but its use is not always permissible as it is very likely that the exchange complex itself may be destroyed. PILLITZ[2] used NH_4Cl as a leaching agent for the first time. He found that by using 1.3N NH_4Cl, complete replacement of cations was possible. GEDROIZ[3] found that N NH_4Cl was suitable for the complete replacement of the cations. KELLEY AND BROWN[4] proposed the use of normal NH_4Cl neutralized to pH 7 with NH_4OH. WILLIAMS[5] then suggested the use of $N/2$ acetic acid for replacing the exchangeable cations.

The determination of exchangeable ions in soils containing $CaCO_3$ is not so simple and straight forward. NH_4Cl dissolves appreciable amounts of $CaCO_3$ so that the Ca in the leachate will represent the exchangeable Ca as well as some Ca derived from the carbonate dissolved. HISSINK[6] used NaCl for determining exchangeable calcium and magnesium in presence of $CaCO_3$.

SCHOLLENBERGER[7] proposed the use of neutral normal ammonium acetate in place of ammonium chloride for the replacement of exchangeable cations from natural exchange materials. Thus, the wide variety of methods available for the determination of exchangeable cations has often necessitated the comparative studies of them so that their relative applicability may be properly assessed. In this paper an attempt is made to present a comparative study of the different methods of determining exchangeable cations in the clay and mica minerals: kaolinite, halloysite, montmorillonite, vermiculite, biotite and muscovite.

EXPERIMENTAL

The cation exchange reactions were carried out as follows:

One gram of the various minerals was shaken with 40 ml of different concentrated salt (B.D.H. AnalaR reagent) solutions and then allowed to stand overnight. Next day the contents of the flask were filtered and the samples were leached with the salt solutions until a definite volume of the leachate was collected. NH_4Cl and CH_3COONH_4 were destroyed from the leachate by evaporation to dryness in presence of conc. HNO_3 and by simple evaporation respectively.

The exchangeable cations in the leachate were estimated as below.

Calcium:	By precipitation as calcium oxalate and volumetric determination.
Magnesium:	By precipitation as magnesium-ammonium phosphate and determination as $Mg_2P_2O_7$ gravimetrically.
Potassium:	By precipitation as potassium cobaltinitrite and volumetric determination.
Sodium:	By precipitation as sodium-uranyl magnesium acetate and then weighing as $Na(UO_2)_3Mg(CH_3COO)_9 \cdot 8H_2O$.

RESULTS

The amounts of exchangeable cations as determined by different methods are shown in Tables I - VI.

TABLE I

MONTMORILLONITE (KASHMIR)

Method	*Exchangeable calcium (m.e./100 g)*	*Exchangeable magnesium (m.e./100 g)*	*Exchangeable potassium (m.e./100 g)*
SCHOLLENBERGER'S CH_3COONH_4 method	77.2	28.09	1.54
KELLEY & BROWN'S NH_4Cl method	76.42	28.50	1.54
GEDROIZ'S NH_4Cl method	71.80	29.82	1.62
WILLIAMS'S CH_3COOH method	68.72	24.67	1.00
HISSINK'S NaCl method	66.31	21.85	—

TABLE II

VERMICULITE (MYSORE)

Method	*Exchangeable calcium (m.e./100 g)*	*Exchangeable magnesium (m.e./100 g)*	*Exchangeable potassium (m.e./100 g)*
SCHOLLENBERGER'S CH_3COONH_4 method	27.20	27.95	2.27
KELLEY & BROWN'S NH_4Cl method	26.58	26.80	2.04
GEDROIZ'S NH_4Cl method	24.30	25.62	2.30
WILLIAMS'S CH_3COOH method	23.71	25.14	1.92
HISSINK'S NaCl method	23.24	26.43	—

References p. 435

TABLE III

MONTMORILLONITE (WYOMING, U.S.A.)

Method	*Exchangeable calcium (m.e./100 g)*	*Exchangeable magnesium (m.e./100 g)*	*Exchangeable potassium (m.e./100 g)*	*Exchangeable sodium (m.e./100 g)*
SCHOLLENBERGER'S CH_3COONH_4 method	27.65	23.17	2.36	29.12
KELLEY & BROWN'S NH_4Cl method	26.81	22.80	2.24	28.78
GEDROIZ'S NH_4Cl method	25.76	22.26	2.85	28.14
WILLIAMS'S CH_3COOH method	24.30	21.76	1.96	22.82
HISSINK'S NaCl method	21.80	22.39	—	—

TABLE IV

BIOTITE (ONTARIO, CANADA)

Method	*Exchangeable calcium (m.e./100 g)*	*Exchangeable magnesium (m.e./100 g)*	*Exchangeable potassium (m.e./100 g)*
SCHOLLENBERGER'S CH_3COONH_4 method	6.80	9.95	8.22
KELLEY & BROWN'S NH_4Cl method	6.14	8.82	7.61
GEDROIZ'S NH_4Cl method	5.82	8.31	6.90
WILLIAMS'S CH_3COOH method	4.32	7.20	6.14
HISSINK'S NaCl method	4.80	6.89	—

TABLE V

MUSCOVITE (VERMONT, U.S.A.)

Method	*Exchangeable calcium (m.e./100 g)*	*Exchangeable magnesium (m.e./100 g)*	*Exchangeable potassium (m.e./100 g)*
SCHOLLENBERGER'S CH_3COONH_4 method	1.10	4.52	2.34
KELLEY & BROWN'S NH_4Cl method	1.10	4.16	2.34
GEDROIZ'S NH_4Cl method	0.89	3.21	1.87
WILLIAMS'S CH_3COOH method	0.72	3.95	2.00
HISSINK'S NaCl method	0.72	3.46	—

TABLE VI

KAOLINITE (JUBBULPORE) AND HALLOYSITE (UTAH, U.S.A.)

Method	*Exchangeable calcium in m.e./100 g* *Kaolinite*	 *Halloysite*
SCHOLLENBERGER's CH_3COONH_4 method	14.50	21.53
KELLEY & BROWN's NH_4Cl method	14.02	20.78
GEDROIZ's NH_4Cl method	14.92	21.86
WILLIAMS's CH_3COOH method	13.71	19.24
HISSINK's NaCl method	11.97	17.10

DISCUSSION

A perusal of the results presented in Tables I - VI, shows the variation in the values of exchangeable cations from different minerals when determined by different methods. As a matter of fact, regardless of the kind of the exchange material, the values of the exchangeable cations depend upon the following factors:

1. Complete exchange of all the cations by some cation not present in the sample.
2. Accurate determination of the cations in the solution.
3. Determination of the cations that pass into solution from soluble substances.

So far as the determination of cations is concerned, the same methods of estimations have been used in all cases and so the second factor does not matter in the variation in values of exchangeable cations. The difference may possibly be due to factors (1) and (3). The values of exchangeable cations as determined by SCHOLLENBERGER's and KELLEY AND BROWN's methods are fairly similar. CH_3COONH_4 is a neutral salt and in KELLEY AND BROWN's method the NH_4Cl solution has been neutralized to pH 7. By using neutral *N* NH_4Cl the exchangeable cations are almost completely exchanged by NH_4 ions. The only difficulty with this neutral *N* NH_4Cl method is the removal of NH_4Cl from the leachate before estimating the cations. CH_3COONH_4 can be removed by gentle evaporation while the leachate has to be evaporated to dryness with conc. HNO_3 in order to decompose NH_4Cl. In the GEDROIZ NH_4Cl method, an acid solution of NH_4Cl is used. So H ions as well as NH_4 ions take part in the exchange reaction. It is also evident from the results that the amounts of exchangeable cations obtained by WILLIAMS's method are much smaller than those obtained by SCHOLLENBERGER's and KELLEY AND BROWN's methods. Perhaps this may be due to the incomplete replacement of cations by CH_3COOH. HISSINK's method gives comparatively lower values of exchangeable calcium. This may firstly be due to the difference in the exchanging powers of sodium and ammonium and secondly to the complete elimination of calcium that might come by a solution process.

As a result of comparative studies of the various methods, it seems that SCHOLLENBERGER's method is quite well suited for cation exchange studies as the ammonium thus adsorbed gives a fairly accurate measure of the base-exchange capacity at pH 7. Comparison of this quantity with the sum of all the cations that are brought into the ammonium salt solution will indicate at once whether or not important amounts of one or more kinds of cations have been brought into solution by some process other than by exchange. Fortunately the determination of base exchange capacity is not influenced by the presence or absence of soluble or decomposable substances.

References p. 435

SUMMARY

A comparative study of the various methods of determining exchangeable cations was made in order to assess their relative applicability. It seems that SCHOLLENBERGER's method is quite well suited for cation exchange studies as the ammonium thus adsorbed gives a fairly accurate measure of the cation exchange capacity at pH 7.

RÉSUMÉ

Une étude comparative a été effectuée des différentes méthodes de détermination des cations échangeables. Il semble que la méthode de SCHOLLENBERGER convient très bien pour les études d'échange de cations: l'ammonium ainsi adsorbé peut donner une mesure assez précise de la capacité d'échange des cations au pH 7.

ZUSAMMENFASSUNG

Die vorliegende Arbeit beschreibt einen Vergleich der verschiedenen Methoden zur Bestimmung von austauschbaren Kationen. Es scheint dass die SCHOLLENBERGER'sche Methode recht gut für Kationenaustausch-Untersuchungen geeignet ist; das adsorbierte Ammonium gibt ein ziemlich genaues Mass der Kationen-Austauschfähigkeit bei pH 7.

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THE PAPER CHROMATOGRAPHY OF SOME MANGANESE AND COPPER VALENCY STATES

by

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INTRODUCTION

Manganese and copper are known to undergo valency changes in biochemical systems; for example Mn in soil bacteria and Cu in the enzymes tyrosinase and ascorbic acid oxidase.

The separation of the valency states of Mn and Cu by paper chromatography was therefore undertaken as a preliminary to a study of possible valency changes of these metals during metabolism.

EXPERIMENTAL

Manganese

The solutions used were prepared as follows:

Mn^{+2}: a saturated solution of $Mn(COOCH_3)_2 \cdot 4H_2O$ in glacial acetic acid was employed.

Mn^{+3}: $Mn(COOCH_3)_2 \cdot 4H_2O$ (3.1 g) was dissolved in glacial acetic acid (10 ml) with warming. Powdered $KMnO_4$ (0.75 g) was added and the mixture boiled for 2 min. It was then cooled and filtered (Whatman No. 41) and the filtrate diluted with glacial acetic acid.

Mn^{VII}: A solution of powdered $KMnO_4$ in glacial acetic acid was prepared with the addition of a few drops of water to increase the solubility of the salt.

Separation of the valencies. These were performed by downward runs on acid-washed Whatman No. 1 paper strips with an eluant prepared by mixing glacial acetic acid (10 ml) with acetic anhydride (30 ml) and running the wet spots as quickly as possible. The blank strips were put into the eluant, and when the liquid front approached the "start line" the mixed Mn^{+2}-Mn^{+3} or Mn^{+3}- Mn^{VII} solutions were spotted on to the paper. This ensured minimum delay before the separation began. It was important not to over-load the strips as this caused tailing to take place.

A run of only 5 cm was necessary to show whether an Mn^{+3} solution contained Mn^{VII} or Mn^{+2}. In the first instance a pink spot above the brown Mn^{+3} spot showed Mn^{VII} but the chromatograms had to be developed to show Mn^{+2}. This was done by dipping them into a solution of "tetrabase" in acetone and drying them. Blue spots appeared for Mn^{+3} and Mn^{VII} at R_F values 0.94 and 0.48 respectively. A blue colour was sometimes observed with Mn^{+2} ($R_F \simeq 0.16$) if it had been run with Mn^{+3}. Mn^{+2} was also detected as a yellow spot by dipping the strip in a solution of oxine in ether, drying it and exposing it to ammonia vapour.

Mn^{+2} and Mn^{VII} interacted to give Mn^{+3} (see preparation of Mn^{+3} above) and so a separation between these two valencies was not feasible. To avoid the reduction of higher Mn valencies on the paper it was essential to exclude ketones, ethers or alcohols from the eluant. Using the given eluant, the Mn^{VII} spot remains moderately stable during a short run (5-7 cm), but tends to reduce gradually to Mn^{+3} and Mn^{+2} giving short forward and backward "tails". This reduction was speeded up if either a stronger (formic) or weaker (propionic) acid was used in the eluant.

Copper

The solutions used were prepared by dissolving Cu_2Cl_2 and $CuCl_2.2H_2O$ in a minimum of $10N$ hydrochloric acid, and diluting the solutions with about ten times their volume of acetone. If it was desired to keep the cuprous solution, it was stored under CO_2.

Separation of the valencies. POLLARD, MCOMIE AND BANISTER[1] reported that Cu^+ and Cu^{+2} could be well separated by ascending paper chromatography using an eluant consisting of ether, methanol, hydrochloric acid and water (50 : 30 : 4 : 15 by volume) which was developed primarily for the separation of uranium valencies. Repetition of these experiments by the author showed that although a good separation was obtained, some oxidation occurred with Cu^+ causing back tailing and a weakening of the final Cu^+ spot on the paper-strip. It was thought that the more polar constituents of the solvent (the acid and water) tended to keep the cuprous copper in ionic form thus rendering it susceptible to oxidation. When a less polar eluant was used and the run was performed in an atmosphere of CO_2, oxidation and tailing were eliminated.

The eluant consisted of ethanol (30 ml), glacial acetic acid (5 ml) and ether (50 ml). About 100 ml of this eluant was poured into the bottom of a chromatographic jar (30 cm × 12.5 cm internal diameter) which contained a trough mounted on a framework. A blank strip of paper was placed in the empty trough and the tank was closed with a greased ground-glass lid through which a small hole (5 mm diam.) had been bored. The tank was then filled with CO_2 through a delivery tube which was inserted through the hole in the lid and allowed to reach the bottom of the vessel. The delivery tube was then withdrawn and the mixed Cu valency solution spotted onto the paper-strip by means of a capillary tube inserted through the hole in the lid. The delivery tube was re-inserted and a little more CO_2 passed; the tube was then finally withdrawn and the hole closed by a cork. The tank was allowed to stand for about 10 minutes and then the eluant was introduced into the trough (through the hole in the lid) using a filter-funnel, the stem of which had been drawn out for the purpose.

After a run of 10-15 cm, the dried strips were developed by spraying them with a solution of Na_2MoO_4 weakly acidified with $2N$ HCl. This showed up Cu^+ as a blue spot ("Mo blue"). The strip was re-dried and dipped into a solution of rubeanic acid in ether followed by exposure to NH_3 when both valencies were shown up as olive-green spots. If air had been effectively excluded from the jar no back-tailing of Cu^+ was observed. Freshly-run strips were also developed by dipping them into either an aqueous solution of potassium ferrocyanide (brownish pink spots for both valencies) or an ethereal solution of oxine followed by exposure to NH_3 (yellow spots). Neither of these reagents however was as sensitive as rubeanic acid. R_F values were approximately 0.2-0.3 for Cu^{+2} and 0.6-0.7 for Cu^+.

Cuprous oxinate. Previous work[2,3] upon the chromatography of Mo and Fe valencies led to the discovery of 8-hydroxyquinoline complexes of these metals in lower valence-states. In view of this finding, it was decided to investigate the possible existence of a Cu^+-oxine complex. This was obtained as follows:

Cu_2Cl_2 was prepared by boiling $CuCl_2$ with copper turnings in an excess of $10N$ HCl and pouring the solution into a tenfold excess of water. The precipitate was washed by decanting it in turn with water, acetone and ether in an atmosphere of CO_2 and dried in a stream of CO_2 at 50-60°. The pure white product was preserved in CO_2 in a sealed tube. Cuprous chloride (0.5 g) and 8-hydroxyquinoline

(3.5 g) were shaken together dry in a stoppered tube containing CO_2. Pyridine (10 ml) was added and the mixture warmed in a slow stream of CO_2 until solution was effected. Into a 350 ml flask, 150 ml of water was poured and all air expelled by a vigorous stream of CO_2. Sodium dithionite ($Na_2S_2O_4$) (1 g) was added, and when dissolved the mixed solution of Cu_2Cl_2 and oxine in pyridine was added and the flask corked and shaken vigorously.

The orange precipitate was filtered off through a Whatman No. 541 filter paper at the pump in an atmosphere of CO_2 by using the simple device illustrated below in Fig. 1. The minimum water pressure was used to pull the filtrate through the funnel as it was important that air should not be sucked into the funnel and oxidise the cuprous complex.

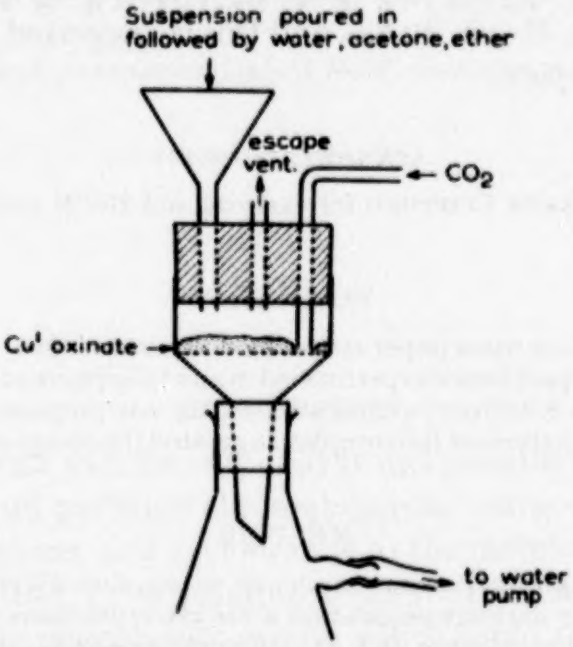

Fig. 1. Simple apparatus for filtration in CO_2.

The contents of the funnel were washed in turn with water, acetone and ether (CO_2 atmosphere), and transferred as quickly as possible to a boiling tube which was fitted with a bored cork carrying inlet and outlet tubes and from which air had been displaced by CO_2. The tube was placed in a water bath at 40-50° and a steady stream of dry CO_2 passed until the complex was a fine, dry, orange powder. This could be preserved in CO_2 in a sealed tube, but when exposed to air the powder oxidised slowly giving green cupric oxinate. The orange complex contained no Cl or S (from $S_2O_4^{-2}$) but only cuprous copper (shown by the chromatographic analysis of a solution of the powder in HCl), oxine, and pyridine (expelled by boiling with NaOH). An analogous preparation of the complex using 25 ml of ethanol instead of 10 ml pyridine as the solvent medium resulted in an orange product which could not be dried without decomposition. It appears therefore that combined pyridine is necessary for the stability of the complex.

ANALYSIS OF THE COMPLEX

Wet-ashing with nitric and perchloric acid resulted in the formation of blue crystals which did not give the reactions of ionic copper. The crystals were decomposed by hot NaOH giving colloidal cupric oxide which could not be filtered. Calcination of the complex caused volatilization and loss of copper. In view of these difficulties, the method of BERG[4] was used as follows:

0.5-0.7 g of the Cu^+ complex was accurately weighed and transferred to a 400 ml beaker with distilled water (30-50 ml); 5 ml of 10 vol. H_2O_2 and 2 ml of a strong solution of NaOH were then added. The beaker was covered with a watch glass and the mixture boiled until the smell of pyridine had disappeared. 10*N* HCl was added drop by drop until the precipitate had just dissolved and the solution, after cooling, was transferred quantitatively to a conical flask. Four times its volume of distilled water was added, followed by an excess of potassium iodide. The liberated I_2 was titrated with $N/_{20}$ $Na_2S_2O_3$ using starch as indicator. A mean value of 16.3% Cu was obtained. The method was checked using cupric oxinate. Found Cu: 18.0 and 18.3. Calc. for $Cu(C_9H_6ON)_2$: Cu, 18.1.

N analyses were done by the micro-method of Dumas. The N content varied according to the method by which the complex was dried.

At 60-70° in CO_2, found N: 7.5. At 40° in CO_2, found N: 7.9. At 40° in pyridine-saturated CO_2, found N: 8.3. Thus it seemed that some N (presumably as pyridine) was lost during the drying process. A check analysis on cupric oxinate gave N: 8.1. Calc. for $Cu(C_9H_6ON)_2$: N, 8.0.

The complete composition of the somewhat unstable cuprous complex was: Cu: 16.3, C: 59.6, H: 3.9, N: 8.3. $(CuC_9H_6ON{\cdot}C_9H_7ON)_2{\cdot}C_5H_5N$ (*cf.* Ag^+ compound[5]) requires Cu: 16.2, C: 57.0, H: 3.6, N: 8.9, and this is suggested by the author as a possible formula for the complex.

ACKNOWLEDGEMENT

The author thanks Mr. DEREK CLIFFORD for carrying out the N analyses on the copper oxinate complexes.

SUMMARY

Chromatographic separations upon paper strips are described for Mn^{+2} and Mn^{+3}, Mn^{+3} and Mn^{VII}, and Cu^+ and Cu^{+2}. The last separation was performed in an atmosphere of CO_2 to prevent the oxidation of Cu^+. An unstable cuprous-8-hydroxyquinoline complex was prepared from cuprous chloride and oxine in pyridine medium. Analysis of the complex suggested the composition $(CuC_9H_6ON{\cdot}C_9H_7ON)_2{\cdot}C_5H_5N$.

RÉSUMÉ

Des séparations chromatographiques sur bandes de papier sont décrites pour Mn^{+2} et Mn^{+3}, Mn^{+3} et Mn^{VII}, Cu^+ et Cu^{+2}. Cette dernière séparation a été effectuée dans une atmosphère d'anhydride carbonique pour empêcher l'oxydation de Cu^+. Un complexe instable Cu(I)-8-hydroxyquinoléine a été préparé à partir de chlorure de cuivre(I) et d'oxine, dans la pyridine. L'analyse de ce complexe donne la composition suivante $(CuC_9H_6ON{\cdot}C_9H_7ON)_2{\cdot}C_5H_5N$.

ZUSAMMENFASSUNG

Die Trennung, durch Chromatographie auf Papierstreifen, von Mn^{+2} und Mn^{+3}, Mn^{+3} und Mn^{VII} und von Cu^+ und Cu^{+2} wurde beschrieben. Die letztere Trennung wurde in Kohlendioxyd-Atmosphäre ausgeführt um Oxydation des Cu^+ zu verhindern. Ein unbeständiger Cupro-8-Hydroxychinolin-Komplex wurde aus Kupfer(I)-chlorid und Oxin in Pyridin hergestellt. Die Analyse dieses Komplexes liess auf die folgende Zusammensetzung schliessen: $(CuC_9H_6ON{\cdot}C_9H_7ON)_2{\cdot}C_5H_5N$.

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THE THEORY AND PRACTICE OF LIQUID-LIQUID PARTITION CHROMATOGRAPHY OF PHENOLS

by

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INTRODUCTION

It was shown by ZAHNER AND SWANN[1] that it was possible to separate phenol from the cresols by liquid-liquid partition chromatography using silica gel as the support, water as the stationary phase, and cyclohexane as the mobile phase. Continuing their work PEARSON[2] showed that, by using aqueous methyl cellosolve, it was possible to separate the lower boiling phenols into groups which could then be resolved by ultra violet absorption analysis.

Comparing these results with those obtained in other fields it was thought that this chromatographic technique could be improved to achieve complete separation so that the eluate could be analysed by a non-specific colorimetric method as an alternative to ultra violet absorption analysis.

EXPERIMENTAL

Repeating the work of the authors quoted above it was found that adsorption chromatography was playing some part in the separations obtained. As this makes the theoretical interpretation of the results rather difficult, preliminary work was directed to finding a system in which adsorption chromatography played no part.

SUPPORT FOR THE STATIONARY PHASE

Efforts to reduce the adsorption of the phenols by the silica gel, which included the preparation and examination of several types of gel were unsuccessful. Of the other materials then examined "Celite 535" was by far the most satisfactory and was therefore more fully tested. A statistical evaluation of this material indicated that with water as the stationary phase and cyclohexane as the mobile phase, a column 20 cm long had an efficiency of 600 theoretical plates.

This series of experiments also showed that although little or no adsorption of the phenol was occurring the elution curves were still tailing rather badly. This was attributed to a variation of the partition coefficient with the amount of phenol present and attention was therefore turned to the stationary phase.

STATIONARY PHASE

It was thought that the use of a buffered stationary phase might reduce the asymmetry of the elution curves[3] and also increase the separation factors[4] (the ratio of α_1 to α_{11} where $\alpha_1 > \alpha_{11}$). The following buffer solutions were therefore tested.

(i) Sodium carbonate solutions when used as the stationary phase gave partition coefficients which were only slightly greater than those for water. This buffer was therefore only of use for the separation of phenol itself, the component with the largest partition coefficient.

(ii) Di-sodium phosphate solutions of 0.5*M* concentration and adjusted to pH 11.6 with sodium hydroxide solution gave a large increase in the values of both the partition coefficient and the separation factors. A comparison of the latter values with those for water is given in Table I.

TABLE I

COMPARISON OF SEPARATION FACTORS

α_1	α_{11}	*Water*	*Phosphate Buffer*
Orthocresol	2 : 6-Xylenol	14.20	20.00
Paracresol	Orthocresol	1.66	3.20
Metacresol	Paracresol	1.14	1.43

This increased separation factor makes possible the complete separation of the three isomeric cresols as reported earlier[5]. Unfortunately it was found that at low ambient temperatures the buffer salt crystallised out on the column reducing the partition coefficients which resulted in the incomplete separation of the cresols.

(iii) Sodium silicate solutions when used as the stationary phase reproduced the separation factors which were found with the phosphate buffer and did not deteriorate with time. In addition it was found that the values of the partition coefficients could be varied by altering the concentration of sodium silicate in the stationary phase.

Some difficulty was experienced in duplicating columns with regard to partition coefficients. This variability was finally traced to the length of time the stationary phase is exposed to the atmosphere when it is in a finely divided condition on the Celite. This difficulty was overcome by standardising the time of mixing of the stationary phase and the Celite prior to the addition of the cyclohexane.

Table II shows the change in the partition coefficient of metacresol with concentration of sodium silicate. The latter was prepared from a sodium silicate solution of S.G. 1.7 ($Na_2O/SiO_2 = 0.5$) and 2.5 ml of the resulting solution was used for the stationary phase on 6.5 g "Celite 535" to give a packed length of 18 cm in a 0.9 cm diameter column.

TABLE II

EFFECT OF SILICATE CONCENTRATION ON PARTITION COEFFICIENT

g Sodium silicate solution S.G. 1.7 per 100 g stationary phase	*Partition coefficient of metacresol*
4	20.0
8	38.0
12	63.0
16[a]	100.0

[a] At this concentration the "Celite 535" is attacked.

With columns shorter than 18 cm smaller partition coefficients than those given in Table II were found. This was attributed to inadequate buffering capacity at the top of the column where the initial concentration of phenol is very high. With columns longer than 18 cm this factor becomes negligible and the partition coefficients constant.

THEORY OF DESIGN OF LIQUID-LIQUID PARTITION COLUMNS

During the course of the investigation many partition coefficients were calculated for phenols between cyclohexane and the buffer solutions from the expression

$$a_2 = \frac{V - a}{b} \qquad (1)$$

where V is the volume in ml which has passed through the column prior to the emergence of the maximum concentration of the phenol, and a and b are the volumes in ml of the mobile and stationary phases respectively.

It was noted that the ratio of the partition coefficients of any two phenols was constant, and independent of the nature of the stationary phase when the latter had a pH above 11. This can be expressed in the general form

$$a_1 = ma_2 + c \qquad (2)$$

where m and c are constant for any two phenols.

The fullest use could not be made of this information until a relationship had been found between the constants of equation (2) for the various phenols and the characteristics of the column necessary for their separation. It was found possible to derive such an expression in the following manner:

Consider two phenols A and B with partition coefficients a_1 and a_2 where $a_1 > a_2$. Thus the first phenol to emerge from the column will be B with elution volume V, followed by A with elution volume P.

Then from equation (1) for phenol A

$$a_1 = \frac{P - a}{b} \qquad (3)$$

for phenol B

$$a_2 = \frac{V - a}{b} \qquad (4)$$

But as

$$a_1 = ma_2 + c \qquad (2)$$

from (3) and (4)

$$\frac{P - a}{b} = m\,\frac{(V - a)}{(b)} + c \qquad (5)$$

As the following equation gives the number of theoretical plates (R) needed for a separation of six standard deviations[6]

$$\frac{R + 3\sqrt{R}}{R - 3\sqrt{R}} = \frac{a + a_1 b}{a + a_2 b} \qquad (6)$$

it follows from (3) and (4) that

$$\frac{R + 3\sqrt{R}}{R - 3\sqrt{R}} = \frac{P}{V} \qquad (7)$$

and substituting for P from equation (5) we obtain

$$R = 9\left[\frac{V(m + 1) - a\,(m - 1) + bc)}{V(m - 1) - a\,(m - 1) + bc)}\right]^2 \qquad (8)$$

and similarly by substituting for V in equation (7) we obtain

$$R = 9\left[\frac{P(m+1) + a(m-1) - bc}{P(m-1) - a(m-1) + bc}\right]^2 \quad \ldots\ldots\ldots\ldots\ldots (9)$$

Thus once the relationship between the partition coefficients of any two phenols is known, *i.e.* the value of m and c in equation (2), this final equation (9) can be used in two ways:

(a) Where a given separation is not particularly difficult and where the time taken for the analysis is critical an arbitrary value for P is chosen. The equation now relates R with the column constants a and b, and as these are determined by the length of the column, assuming a constant cross sectional area, then a relationship between R and the length of the column is obtained. By substituting values of a and b corresponding to 10, 20, 30 cm column lengths in the equation the number of plates required for complete separation on the various lengths of column is obtained. As the number of plates attainable in practice with the various column lengths is known, the selection of the correct length of column is relatively easy. When the correct column length has been selected the concentration of the stationary phase required is found by substituting P together with the appropriate values for a and b in equation (3). From this the partition coefficient required is calculated and the appropriate concentration of silicate found by referring to Fig. 2.

This use of equation (9) may be illustrated by reference to the separation of meta and paracresols. If 50 ml is selected as the value for P and values of a and b for increasing column length are substituted in the equation, the curve shown graphically in Fig. 1 is obtained. The values for the number of theoretical plates found in practice is shown as a straight line on the same figure. It can be seen that when metacresol is eluted at 50 ml it will only be separated from paracresol on column lengths between 11 and 51 cm.

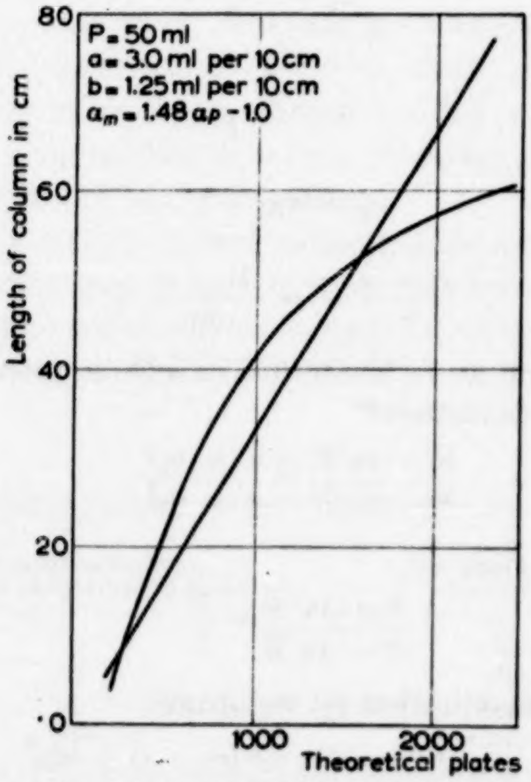

Fig. 1. Relationship between calculated values of R and those obtained in practice.

(b) Alternatively, where a difficult separation is required a and b are chosen to correspond to a reasonably long column. The equation now relates R and P, and the number of theoretical plates required to effect the separation for any given value of P may be calculated. At some value of P this calculated value of the number of plates required will be equal to the experimentally determined number of plates of the column. This or a greater value for the elution volume will permit the separation of the two components. Table III shows the results of such a calculation for the separation of meta and paracresol, where the following constants are used:

Column Length 20 cm
a 6.5 ml
b 2.5 ml
Efficiency 750 theoretical plates
Value for equation (2) $\alpha_m = 1.48\ \alpha_p - 1.0$

TABLE III

RELATIONSHIP BETWEEN P AND R FOR A GIVEN COLUMN

P ml	*R (calculated)*
15	6610
20	1730
30	745
40	535
50	445

It is obvious that the elution volume P should be greater than 30 ml to effect the separation. In practice the value of P may be altered by changing the composition of the stationary phase (refer to previous section).

In the absence of some means of continuous measurement of phenol in the eluate the latter must be cut into bulk fractions. As some latitude must be allowed at the cut point when these are taken, a larger value for R than the one calculated must be used. Alternatively, values greater than three may be substituted in equation (6) dependent upon the value of P.

This method of calculating the dimensions of the column required for a given separation should be applicable to all mixtures of acids or bases where a buffered stationary phase is used, and should remove the practice of this form of chromatography from the field of trial and error.

SEPARATION FACTORS

The following table which gives the separation factor for meta and paracresol shows that above a certain value the separation factor is fairly constant.

TABLE IV

VARIATION OF SEPARATION FACTOR WITH PARTITION COEFFICIENT

α_m	α_p	*Separation factor*
5.3	4.5	1.18
12.1	8.5	1.42
13.0	9.0	1.44
20.9	14.1	1.48
27.0	18.9	1.49
32.0	22.0	1.46

This follows from equation (2) and may also be predicted from ALBERT's equation[7] which correlates the percentage ionisation with the pK of the compound and the pH of the medium. Therefore with a reasonable degree of accuracy equation (2) may be expressed as

$$\text{Log } a_1 = \text{Log } a_2 + \text{Log } m$$

and Fig. 2 shows the relationship when the logarithms of the partition coefficients of the lower boiling phenols are plotted against the logarithm of the partition coefficient of metacresol.

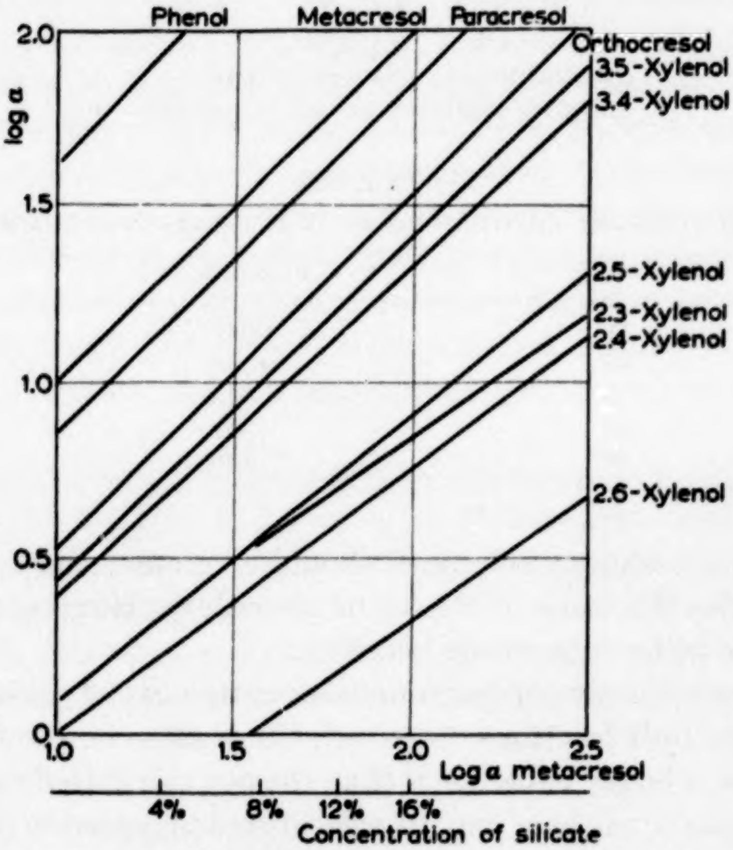

Fig. 2. The relationship between the logarithms of the partition coefficients.

With the aid of this graph and equation (1) it is possible to predict the elution volume of all these phenols on a column when the elution volume of only one phenol is known. For example if the logarithm of the partition coefficient of orthocresol is 1, then that of metacresol is 1.5, and that of 2 : 5-xylenol 0.5, etc.

METHODS

The two analytical methods which follow were designed to give the maximum separation in the shortest possible time using equation (9) to calculate these optimum conditions. The methods should be applicable to the routine determination of phenol and the three cresols, for although the initial packing of the columns is time consuming, thirty or more determinations may be carried out on one column.

Some separation of the higher boiling tar acids is possible and by using a 30 cm column all the six isomeric xylenols have been separated, but it appears doubtful whether such a separation could be anything more than a research tool. The efficiency required, approximately 2,000 theoretical plates, is difficult to achieve and there appears to be a large personal factor in the packing of such high efficiency columns. These separations do suggest however that liquid partition chromatography is a more powerful technique than is generally realised and it is probable that further studies would result in the achievement of greater column efficiencies.

When the phenols have been separated there still remains the problem of estimating the individual phenols in the fractions. For this purpose any non specific colour reaction may be used and such a colorimetric method is given for the determination of phenol. Similar colorimetric methods could be applied to the cresols but where an ultra-violet spectrometer is available this should be used.

1. The determination of phenol in mixtures of coal tar acids

Applicability

The method is applicable to all tar acid mixtures containing not less than 0.5% phenol and to phenol concentrates.

Apparatus

1) Chromatographic column 15 cm × 0.9 cm with a 250 ml bulb and suitable arrangements for applying pressure to the top of the column. (Less than 10 lbs per sq. inch.)
2) Stoppered 25 ml cylinders.
3) Stop watch.

Reagents

1) "Celite 535" which has been treated overnight with concentrated HCl, washed to neutrality and dried at 140°C (Johns Manville).
2) 1*M* Sodium carbonate solution.
3) 0.5*M* Sodium hydroxide solution.
4) McIlvaine's buffer solution pH 7.
5) N.N.C.D. Reagent — 2-chloro-4-nitro-benzene-diazonium naphthalene-2-sulphonate (Hopkin and Williams No. 3090). Dissolve 0.02 g in 250 ml distilled water not more than half an hour before use.
6) Cyclohexane (sufficiently pure if U.V. analysis is to be used) is shaken with sodium carbonate solution and stored over the carbonate solution.

Packing the column

1 ml of the sodium carbonate solution is thoroughly stirred into 3.25 g of the prepared Celite for 4 minutes. This mixture is made into a slurry by adding cyclohexane and packed according to the method given by MARTIN[8]. A small porcelain bead is the most convenient plug for the lower end of the column, as those of cotton wool tend to absorb phenols.

Testing the column

Prior to using for the first time, and at appropriate intervals afterwards, the column should be tested as in the procedure, and the two ml fractions between 8 and 14 ml should contain no tar acid. A suitable test mixture is 5% w/w phenol in metacresol.

Procedure

That quantity of sample which will contain from 7 to 23 mg of phenol is weighed out and made up to 100 ml in a graduated flask with cyclohexane. 0.3 ml of this solution is added to the column when the level of the cyclohexane has just sunk to the level of the top of the packing. Pressure is applied to column and when the sample has sunk into the packing, two 0.3 ml portions of the cyclohexane are applied in a similar manner to ensure that all the sample is on the column. Approximately 30 ml of the cyclohexane is added to the column and the pressure adjusted to give a flow rate of 1 ml per minute. The eluate is measured from the time of the addition of the sample and the fraction from 14-24 ml is taken for analysis.

Colorimetric analysis

Four ml portions of the fraction 14-24 ml are added to two stoppered cylinders and four ml of the cyclohexane is added to the third cylinder, for use as a blank when measuring the optical density. 10 ml of the buffer solution is added to each cylinder and the contents mixed by gentle agitation.

10 ml of the freshly prepared N.N.C.D. reagent is then added to each cylinder and the contents gently agitated for one minute. Ten minutes after the addition of the N.N.C.D. reagent 2 ml of the sodium hydroxide solution is added and the contents again shaken for one minute. The contents of the cylinder are allowed to settle and the cyclohexane is pipetted from the aqueous layer. The optical density of the latter is measured in a 2 cm cell using an Ilford filter 603. From the mean of the two optical densities the phenol content is determined from a previously prepared calibration graph.

RESULTS

Results of the determination of phenol using the colorimetric method for analysing the eluate are given in Table V.

TABLE V

RESULTS OF DETERMINATION OF PHENOL

Sample		% *by wt. Run 1*	% *by wt. Run 2*	% *by wt. Run 3*
40-42% metacresol	A	2.93	2.94	2.93
Purified orthocresol	B	0.77	0.68	0.67
A with added phenol	C	14.7	14.7	14.8
A calculated from	C	3.0	3.1	3.1

Three samples of high phenol content were analysed by S.T.P.T.C. Test Serial No. 14-50 and the results compared with those given by the method, using U.V. absorption for the analysis of the eluate. The results are shown in Table VI.

TABLE VI

RESULTS USING U.V. ANALYSIS FOR ELUATE

	Method % *by wt.*	*S.T.P.T.C.* % *by wt.*
Sample A.[C.P. 28.5]	79.0	78.3
Sample B.[C.P. 31.8]	84.6	84.0
Distilled crude carbolic acid	36.2	36.0

2. *The determination of ortho-, meta- and para-cresol in cresol fractions*

Applicability

The method is applicable to tar acid mixtures with less than 2% phenol (see note 1), and negligible amounts of material boiling above 215°C.

Apparatus

1) As in the method for the determination of phenol except that the column is 25 cm long.
2) U.V. Spectrometer.

Reagents

1) "Celite 535" as previously described.
2) N.N.C.D. reagent as previously described.
3) 0.5M Sodium hydroxide solution.
4) Solution of sodium silicate S.G.1.7. (Hopkin and Williams 8080), 5 g made up to 100 g with distilled water.
5) Cyclohexane sufficiently pure for use with U.V. Spectrometer.

Packing the column

As in the previous method except that 6.5 g of Celite is used with 2.5 ml of the sodium silicate solution as the stationary phase. The column should be approximately 20 cm long.

Testing the column

A suitable test mixture is one with equal parts of the three cresols. A qualitative colorimetric test on each 2 ml fraction should give two fractions between the meta- and para-cresols which contain no tar acid. Fig. 3 shows the result of such a test where the optical density of the fractions has been measured.

As some variability is found in the silicate quoted above the cresols may not occupy the positions shown in Fig. 3. In this case a further column is packed using a greater or small concentration of sodium silicate in the stationary phase. Our results suggest that the correct concentration will lie between 4% and 7% w/w sodium silicate.

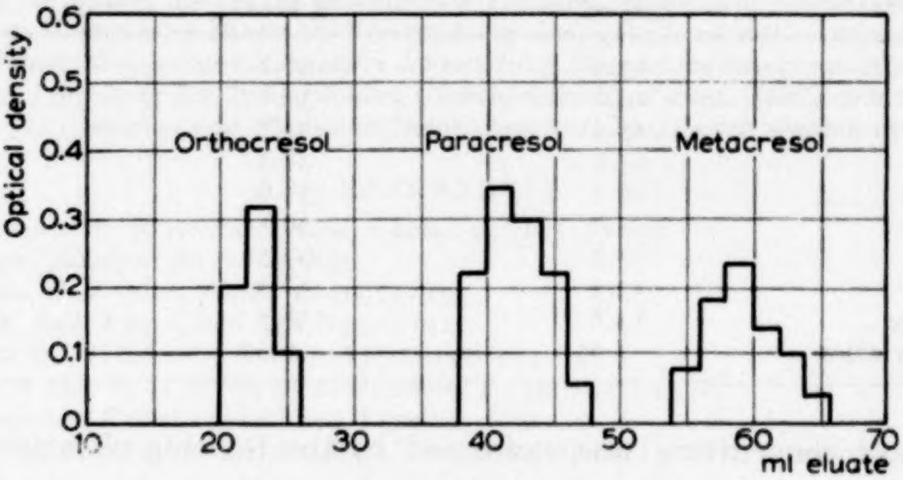

Fig. 3. Test run on 20 cm column.

Procedure

That quantity of sample which will contain approximately 0.03 g of metacresol is weighed out and made up to 100 ml in a graduated flask with cyclohexane. 0.3 ml is added to the column as in the previous method and the rate of elution adjusted to 0.5 ml per minute.

To obtain bulk fractions which only contain one cresol, the course of the chromatogram is followed by spot testing with the N.N.C.D. reagent. Three drops of the latter reagent are added to one drop of eluate and, after mixing, three drops of the sodium hydroxide solutions are added. If any phenol is present a colour will develop which is red in the case of ortho- and metacresol, purple with paracresol. With a little practice it is possible to cut the eluate between the meta- and paracresols. The position of the tar acids is affected by temperature as shown in Fig. 4. The bulk fractions are weighed, corrected for the amount used for spot testing and the amount of cresol present in each fraction is determined by U.V. spectrometry using a 4 cm cell.

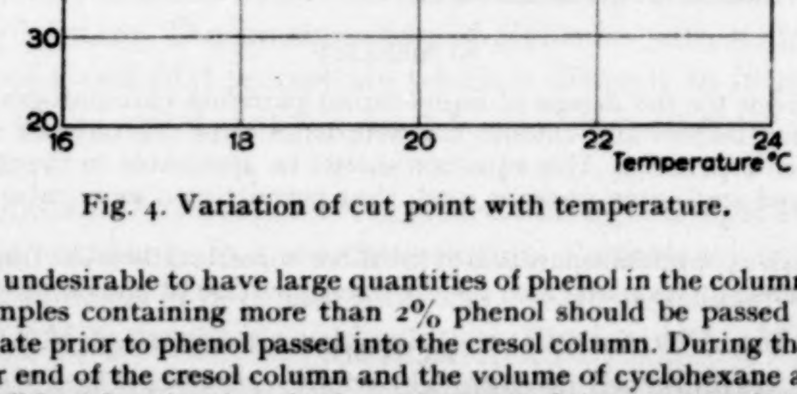

Fig. 4. Variation of cut point with temperature.

Note 1. Since it is undesirable to have large quantities of phenol in the column because of its large elution volume, samples containing more than 2% phenol should be passed through the phenol column, and the eluate prior to phenol passed into the cresol column. During this process vacuum is applied to the lower end of the cresol column and the volume of cyclohexane above the packing is kept as small as possible. After the phenol column is removed the amount of phenol present may be determined as in the first method.

References p. 449

RESULTS

Table VII shows the results of eight determinations on a commercial meta-rich cresylic acid.

TABLE VII

RESULTS OF EIGHT ANALYSES OF A CRESYLIC ACID

Run No.	*Orthocresol % by wt.*	*Metacresol % by wt.*	*Paracresol % by wt.*
1	13.2	38.2	29.7
2	14.2	39.1	29.6
3	13.4	38.3	29.6
4	13.7	38.3	29.1
5	16.2	38.6	31.3
6	13.8	39.1	29.6
7	12.8	37.5	28.5
8	13.3	38.5	29.5
Average	13.8	38.5	29.5
Standard deviation	1.05	0.52	0.83

A metacresol concentrate was examined by the Raschig nitration method, I.R absorption and the chromatographic method, the results of which are shown in Table VIII.

TABLE VIII

Method	*I.R.*	*Raschig*	*Chromatography*
Result	70.0%	70.5%	71.3%

A synthetic mixture made up from the purest materials available and the results of two determinations are shown in Table IX.

TABLE IX

ANALYSIS OF SYNTHETIC MIXTURE

	Orthocresol % by wt.	*Metacresol % by wt.*	*Paracresol % by wt.*	*Total % by wt.*
Sample as prepared	33.62	35.04	31.34	100.00
Run 1	32.7	34.6	32.0	99.3
Run 2	33.0	35.0	31.4	99.4

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SUMMARY

An equation is given for the design of liquid-liquid partition chromatographic columns which relates the separation factors and column characteristics with the number of theoretical plates required for a desired separation. This equation should be applicable to the separation of acids or bases when a buffered stationary phase is used, thus permitting a more rational approach to this technique.

Using this approach a complete separation of the three isomeric cresols has been achieved. Methods are given for this determination and also for the determination of phenol in tar acid mixtures.

RÉSUMÉ

Une équation est proposée pour la construction de colonnes de chromatographie de partage liquide-liquide, où les facteurs de séparation et les caractéristiques de la colonne sont liés au nombre de paliers théoriques nécessaires pour une séparation. Il devrait être possible d'appliquer cette équation aux séparations d'acides ou de bases en utilisant une phase stationnaire tamponnée. On a pu par cette méthode, séparer complètement les trois isomères du crésol. On en décrit le mode opératoire, ainsi que celui du dosage du phénol dans des mélanges d'acides du goudron.

ZUSAMMENFASSUNG

Für den Bau von Säulen für die Flüssigkeit-Flüssigkeits-Verteilungschromatographie wird eine Gleichung gegeben, welche die Verteilungsfaktoren und Säulen-charakteristik mit der Anzahl theoretischer Stufen verbindet, die für die gewünschte Trennung nötig sind. Diese Gleichung sollte für die Trennung von Säuren oder Basen bei Verwendung einer gepufferten stationären Phase anwendbar sein und auf diese Weise eine rationellere Anwendung dieser Arbeitstechnik erlauben. So konnte eine vollständige Trennung der drei isomeren Cresole erreicht werden. Methoden für diese Bestimmung und auch für diejenige von Phenol in Gemischen von Teersäuren werden mitgeteilt.

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THE DETERMINATION OF COBALT IN COBALT-PLATINUM ALLOYS

by

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INTRODUCTION

The interest in cobalt-platinum alloys as magnetic materials has necessitated the development of a suitable technique for their analysis.

The precipitation of platinum metal with base metals such as magnesium and zinc proved unsatisfactory because of the tendency of the cobalt and the base metal to accompany the platinum. The precipitation of platinum with hydrogen sulfide from acid solution gives a colloidal precipitate which is difficult to filter. If the platinum sulfide is ignited to the metal, a factor must be used to correct for incomplete volatization of the sulfur.

The work of KRAUS and co-workers[1,2] suggested that a good separation could be made by means of an ion exchange in a chloride solution. Preliminary experiments showed that the chloro complexes of both platinum and cobalt were adsorbed on a column of "Dowex 1" from $9M$ hydrochloric acid solution. Elution with $3M$ hydrochloric acid removes the cobalt and leaves the chloro-platinate on the column.

Further investigation into the reduction of platinum showed that reduction was possible in a sulfuric acid solution with hydrazine sulfate. The ignited platinum was not contaminated with cobalt or salts from solution and the filtrate was suitable for the electrodeposition of cobalt.

PROCEDURE

(a) Separation by ion exchange

Dissolve a sample in aqua regia to give 25 to 100 mg of cobalt. Remove the nitric acid by evaporation to dryness on a steam bath and take up the resultant chlorides with $9M$ hydrochloric acid. Transfer the solution of the chlorides to an ion exchange column (1 cm diameter) containing 10 g of "Dowex 1 × 4", 50-100 mesh, chloride form. Wash the sides of the column with $9M$ hydrochloric acid to fix all of the sample on the column. Elute the cobalt with $3M$ hydrochloric acid into a 400 ml beaker. Add 6 ml of 1 : 1 sulfuric acid and evaporate to fumes of sulfuric. Cool, cautiously add 100 ml of water, and neutralize with ammonium hydroxide. Proceed as described under cobalt electrodeposition.

(b) Separation with hydrazine sulfate

Dissolve a sample in aqua regia to give 25 to 100 mg of cobalt. Add 6 ml of 1 : 1 sulfuric acid and evaporate to fumes. Cool and cautiously add 100 ml of water. Warm to dissolve the sulfates and add 2 g of hydrazine sulfate. Cover the beaker, heat until a vigorous evolution of gas begins, and digest at the boiling point for one hour. Cool, filter through a medium, ashless filter paper, and wash with water. The precipitate may be ignited and weighed as metallic platinum. The filtrate is neutralized with ammonium hydroxide and electrolyzed for cobalt as described below.

ELECTRODEPOSITION OF COBALT

The procedure for the cobalt electrolysis is essentially the same as that of TORRANCE[3] for electrodeposition of nickel.

To the solution from either procedure (a) or (b), add 20 ml of conc. ammonium hydroxide, two g of sodium sulfite and sufficient water to give approximately 300 ml of solution. Electrolyze at 70°-90°C (not less than 70°C) with platinum electrodes at a controlled potential of —0.80 V *vs.* S. C. E. After 15 minutes, increase the potential to —0.85 V *vs.* S. C. E. The total time for electrolysis should be about 25-30 minutes. The residual current is approximately 20 mA. The electrodeposition of cobalt is subject to the normal interferences of controlled potential deposition of cobalt.

DISCUSSION

The separation of cobalt and platinum by hydrazine or ion exchange is superior to separation with hydrogen sulfide or base metal. The precipitation of platinum by hydrazine gives a platinum precipitate which is not contaminated with cobalt or nonvolatile salts. The precipitate is easily filtered and the filtrate is suitable for a subsequent cobalt determination by electrolysis. The ion exchange separation for the determination of cobalt avoids the filtration of platinum sulfide and the removal of sulfide ions following hydrogen sulfide precipitation of platinum. Neutralization of the eluate containing the cobalt with ammonium hydroxide plus an appropriate excess provides a buffered solution suitable for titration with EDTA.

Attempts to elute the chloroplatinate were unsuccessful. Successive samples were passed through the resin until the chloroplatinate was within a few cm of the bottom of the column. The resin was then removed and the column recharged.

The controlled potential electrolysis method was used for cobalt because a superior deposit was obtained than with constant current methods.

Table I lists the results on two cobalt-platinum alloys and a composite powder.

References p. 451

Samples one to five are taken from homogenized ingots. Samples six to sixteen are from a composite powder. High-purity platinum powder and rondel cobalt were used to make the ingot and powder composite[4].

TABLE I

Sample no.	*Method of separation*[a]	*% Co added*	*% Co found*
1	I	11.4	11.4
2	I	11.4	11.8
3	H	11.4	11.4
4	I	28.4	28.3
5	I	28.4	28.5
6	H	23.1	23.1
7	H	23.1	23.1
8	I	23.1	22.7
9	I	23.1	22.8
10	I	23.1	22.8
11	I	23.1	23.1
12	I	23.1	23.0
13	I	23.1	23.2
14	I	23.1	23.2
15	I	23.1	22.8
16	I	23.1	22.9

[a] I = Ion exchange.
H = Hydrazine reduction.

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SUMMARY

The separation and analysis of cobalt-platinum alloys by ion exchange or hydrazine reduction are superior to the usual techniques of hydrogen sulfide precipitation or base metal reduction. Cobalt is determined by controlled potential electrodeposition.

RÉSUMÉ

La séparation et l'analyse des alliages cobalt platine par échange d'ions et par réduction au moyen de l'hydrazine sont plus avantageux que les techniques habituelles par précipitation à l'hydrogène sulfuré ou par réduction métallique. Le cobalt est dosé par électrolyse à potentiel réglé.

ZUSAMMENFASSUNG

Die Zerlegung und Analyse von Kobalt-Platin-Legierungen durch Ionenaustausch oder Hydrazinreduktion sind den üblichen Verfahren durch Schwefelwasserstofffällung oder Metallreduktion überlegen. Das Kobalt wird durch elektrolytische Abscheidung bei geregeltem Potential bestimmt.

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DETECTION AND COLORIMETRIC DETERMINATION OF THE CrO_4^{-2} ION WITH *o*-DIANISIDINE

by

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In previous papers an account has been given by one of us on the applications of *o*-dianisidine in qualitative as well as in quantitative analysis[1].

In the present work, the optimum conditions for the determination of Cr(VI) have been studied. As has been previously pointed out, colour depends on the pH; when the pH value is greater than 2.8 the colour obtained is green, and when it is lower than 2.8 the colour is red. It has also been proved that for pH values between 1.2 and 2.7 the colour intensity remains unchanged and does not depend on the acid used on acidifying. Fig. 1 shows the variation of the extinction at 430-480 mμ with the pH. The sharp change that can be observed at pH 2.8 corresponds to the development of the bluish-green coloration.

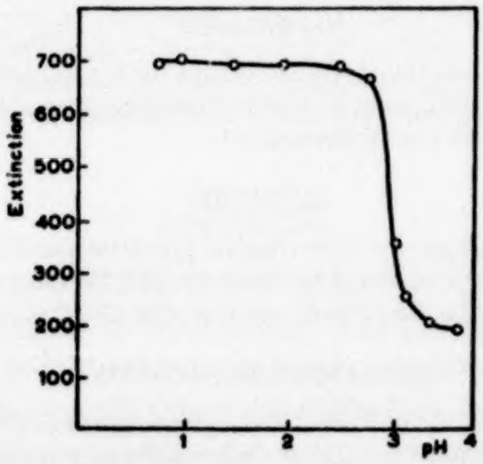

Fig. 1. Variation of the extinction with the pH at 430-480 mμ

It has been observed that the development of colour takes place during a period which reaches its peak-intensity after five minutes. This peak-intensity is not altered during the following twenty minutes, thus affording a long period for the performance of the readings.

Fig. 2 shows the absorption spectrum of the colored solution obtained after addition of 0.5 ml of a 1% acetic solution of *o*-dianisidine to a potassium chromate solution, followed by acidification with 2 ml of $2N$ H_2SO_4. As can be seen, there is only one main absorption band at 450 mμ wave-length.

Reference p. 454

Fig. 3 shows the variation of the extinction (at 430-480 mμ) with the potassium chromate concentration, especially in the range near the perceptibility limit, which is 0.6 γ/ml, to which corresponds a dilution of $D = 10^{-6.2}$; at this concentration range Beer's law remains valid.

All these results lead to the establishment of a sensitive method for the determination of chromate. The accuracy is of 1.5%.

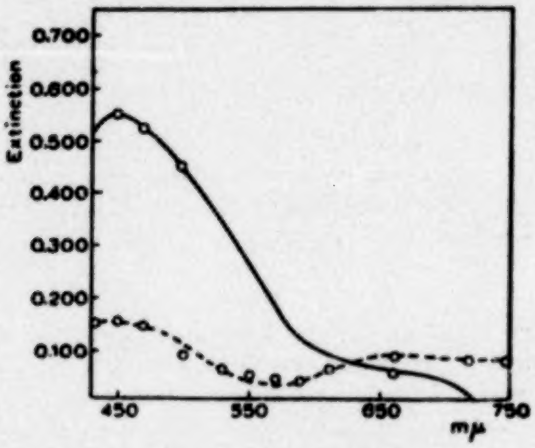

Fig. 2. Variation of the extinction with the wave-length at 3.7 pH and at 1.2 pH.

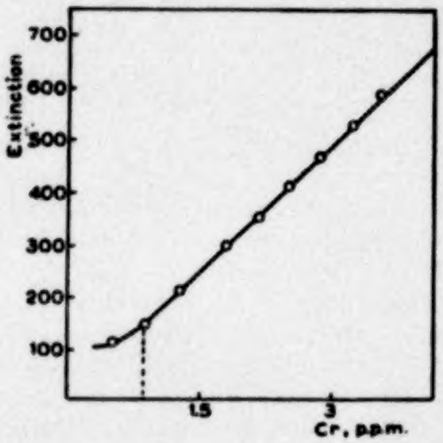

Fig. 3. Variation of the extinction with the potassium chromate concentration (Cr in p.p.m.) at 430-480 mμ.

This reaction can also be used for the qualitative detection of the chromate ion provided that there are no other oxidizing agents present, *e.g.* in the detection of Cr(VI) in the third group of metal ions in the usual systematic qualitative procedure.

The sensitivity is $D = 10^{-6.3}$ ($1 : 2.10^6$), that is about the same order or even greater than the sensitivity of the reactions for the above mentioned anion recommended with diphenylcarbazide ($D = 10^{-6.8}$), strychnine ($D = 10^{-6}$) and chromotropic acid ($D = 10^{-4.7}$)[1].

EXPERIMENTAL

Reagents

Potassium chromate. Analytical reagent, dried at 120°C for two hours; after this time constant weight was obtained. A solution was prepared with a concentration of 3.7346 g of K_2CrO_4 per liter which corresponds to a 1 g chromium/l content. With adequate dilution (30 : 1000) a solution can be obtained having a concentration of 30 mg Cr/l.

Acetic acid. Analytical reagent.

Sulfuric acid. 2*N*.

o-Dianisidine solution. 1 g of *o*-dianisidine is dissolved in the smallest possible amount of hot concentrated acetic acid (2 ml are sufficient); the volume is then made up with water to 100 ml and the solution is filtered. The solution thus obtained usually shows a coloration and it is necessary to treat it with a small portion of activated carbon, and to heat and filter it successively as many times as necessary to obtain either a colorless solution or a very slightly colored one; two or three treatments are usually enough. (Technical *o*-dianisidine, used as an intermediate product in the dyestuff industry, has been employed.)

Apparatus

An Engel filter-photocolorimeter (Kipp & Zonen) covering the visible spectrum from 420 to 785 mμ and an A 75 galvanometer from the same firm, with a sensitivity of 3.10^{-10} amp/mm in the scale have been used. The work has been carried out at the maximum sensitivity of the apparatus; calibrated test tubes were used as well as cuvettes, the thickness of which varied from 5 to 20 mm.

QUANTITATIVE DETERMINATION OF CrO_4^{-2}

Potassium chromate solution containing 0.112 g of K_2CrO_4 per liter, which corresponds to a concentration of 30 γ of chromium per ml is poured down from a microburette into 25 ml calibrated flasks; 0.5 ml of acetic solution of *o*-dianisidine is then added and finally 2 ml of 2*N* H_2SO_4. The volume is made up to 25 ml with distilled water.

The solution is set aside for 5 minutes after the addition of the reagent. Readings can be undertaken in the photocolorimeter, by means of filter 45 which shows its transmission maximum at 450 mμ. Cuvettes with optical thicknesses from 0.5 to 1.6 cm are used according to the chromium concentration of the sample in order to obtain galvanometer readings in the area of the peak-sensitivity of the apparatus.

QUALITATIVE INVESTIGATION OF CrO_4^{-2}

Procedure (in microtube). A few drops of the 1% acetic solution of *o*-dianisidine are added to the CrO_4^{-2}-containing solution; a blue precipitate or a blue coloration appears at once, according to the concentration; the coloration as well as the precipitate take a red color upon acidification (pH under 2.8) and the precipitate then dissolves. This reaction can also take place on filter paper, although the sensitivity is lower.

Sensitivity and *specifity*. In micro test-tube $D = 10^{-6.3}$ $(1:2.10^6)$; on filter paper $D = 10^{-5.3}$ $(1:2.10^5)$. Metallic ions such as Pb, Bi, Cd and As do not interfere in the reaction in the ratio 100/1. The sensitivity decreases somewhat when Sb, Sn and Pt are present (in the case of Pt, it is due to the usual colour of its solutions). Al, Cr, Ni, Co and Zn do not interfere, even in large amounts. Fe^{+3} gives a similar coloration, although it can be masked by a previous addition of F^-. Au^{+3}, Ce^{+4}, OsO_4^{-2}, VO_3^-, $[Fe(CN)_6]^{-3}$ can interfere as they give a similar reaction.

SUMMARY

A new method is described for the colorimetric determination of CrO_4^{-2}; the reagent used is an acetic solution of *o*-dianisidine, which gives a red coloration upon acidification. The procedure is described, the limit of perceptibility being of 0.6 γ/ml. Down to this concentration, the coloration still obeys Beer's law and permits the determination with a 1.5% accuracy. Qualitative investigation of the chromate ion with the above mentioned reagent is also reported. Sensitivity is $D = 10^{-6.3}$.

RÉSUMÉ

Les auteurs proposent une nouvelle méthode pour le dosage colorimétrique de l'anion chromique. Le réactif utilisé est l'*o*-dianisidine, en solution acétique, donnant une coloration rouge, en milieu acide. La limite de perceptibilité est de 0.6 γ/ml (limite de dilution $D = 10^{-6.2}$). A cette concentration la coloration suit encore la loi de Beer et la précision est de l'ordre de 1.5%. La recherche qualitative de l'ion chromique avec ce réactif est également décrite. La sensibilité atteint $D = 10^{-6.3}$.

ZUSAMMENFASSUNG

Die Verfasser berichten über eine neue Methode zur kolorimetrischen Bestimmung von CrO_4^{-2}, unter Verwendung einer essigsauren Lösung von *o*-Dianisidin als Reagens, mit welchem in saurem Medium Rotfärbung auftritt. Die Mitteilung beschreibt den technischen Vorgang und stellt fest, dass die Grenze der Wahrnehmbarkeit bei 0.6 γ/ml liegt, die einer Verdünnungsgrenze von $D = 10^{-6.2}$ entspricht. Unter diesen Voraussetzungen folgt die Färbung noch dem Beer'sche Gesetz. Die Genauigkeit der Bestimmungen beträgt 1.5%.

Es wird ebenfalls der qualitative Nachweis des Chromations mit genanntem Reagens beschrieben, welches eine Empfindlichkeit von $D = 10^{-6.3}$ aufweist.

REFERENCE

[1] *Tables of reagents for inorganic analysis*, 3rd report, International Committee on new analytical reactions and reagents of the "Union internationale de Chimie", Istra, Paris, 1948, p. 89.

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RAPID AND ACCURATE TITRATIONS WITH A CONVENIENT AND COMPACT AUTOMATIC DERIVATIVE SPECTROPHOTOMETRIC TITRATOR

by

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INTRODUCTION

Recently MALMSTADT AND ROBERTS[1] described an automatic titrator which used spectrophotometric detection and a derivative control unit[2,3] to terminate the flow of titrant from a buret at the end-point of a titration. MALMSTADT AND ROBERTS also used the same detection and control system in combination with electrolytic generation of titanous ions for the completely automatic titration of iron[4] and titanium[5] in titanium sponge, alloys and ores. The previously described titration instrument utilized a small grating monochromator and a logarithmic photomultiplier detector. The titration cell compartment was designed originally for use with electrolytic generation of titrant, and it was inconvenient to insert and remove the titration vessel if the titrant was added from a buret. In order to provide a more compact, simple and easy-to-use instrument for rapid automatic titrations, a new spectrophotometric attachment was constructed and is described in the following section on instrumentation.

Most common visual indicator titrations can be automatically performed with the relatively simple titration system described herein, consisting of a convenient spectrophotometric attachment and the commercially available Sargent-Malmstadt second derivative control unit[3]. This instrumental combination is suitable for a wide variety of automatic titrations because the well known indicator procedures can often be used directly with no modifications and usually with few, if any, pretitration considerations and instrument adjustments.

In order to test the instrument and illustrate its general usefulness, several different oxidation-reduction and acid-base titrations using typical indicators were automatically performed and the results are presented. As an aid for adapting existing visual color titrations or developing new titrations for use in the automatic derivative spectrophotometric instrument, the general titration requirements are discussed.

INSTRUMENTATION

The basic components of the automatic derivative spectrophotometric titrator are shown in the block diagram, Fig. 1. Radiation from a tungsten light source passes through a transmission filter in order to isolate a narrow wavelength band which is characteristic of the selected indicator, and passes through the titration solution, and then falls on a simple inexpensive light detector, such as a barrier layer or photoconductive cell. The output of the light detector is fed directly to the Sargent-Malmstadt control unit[3,6] which consists of two sections. One section amplifies and computes a voltage signal proportional to the second derivative of the light detector output; the other section contains a relay system which utilizes the derivative output to activate the buret valve and terminate the flow of titrant at the rapid absorbance change of the indicating material.

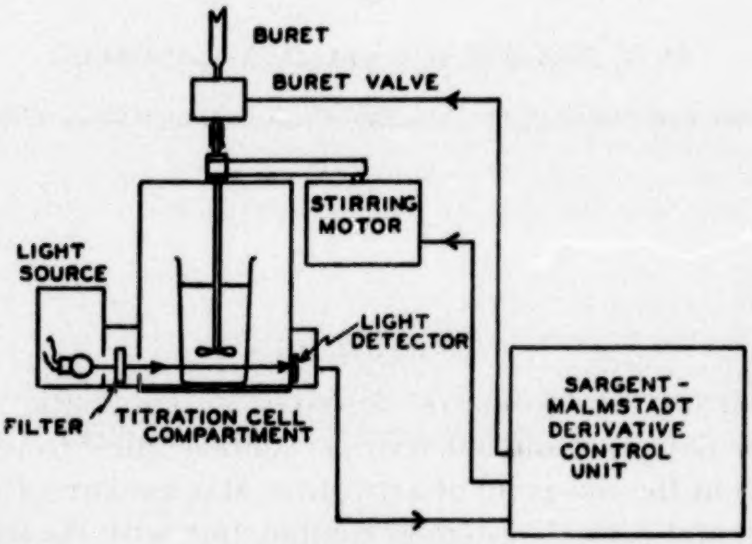
BURET
BURET VALVE
STIRRING MOTOR
LIGHT SOURCE
LIGHT DETECTOR
FILTER
TITRATION CELL COMPARTMENT
SARGENT - MALMSTADT DERIVATIVE CONTROL UNIT

Fig. 1. Block diagram of basic components for the automatic derivative spectrophotometric titrator.

Other end-point control devices are possible, of course, but the derivative system has definite advantages for many titration methods. It reduces or eliminates the pretitration considerations and manipulations usually required for control systems operating at pre-set absorbance values. The advantages of the derivative control system for automatic spectrophotometric and potentiometric titrations were discussed previously[1,2,7,8].

Titration cell compartment

A titration cell compartment was constructed as shown in Fig. 2. The compartment was made from a 4" diameter, 6" long black plastic cylinder A with an aluminum top cover B and an easily removable bottom plate N. When the holes for the stirrer and other mountings had been drilled, the top B was screwed securely to the stirring unit from the Sargent-Malmstadt automatic titrator. Support brackets were mounted on cylinder A perpendicular to the light path, and these brackets connected to the motor and buret stand. The titration cell compartment and motor formed a compact unit which could be adjusted to any height on the stand to permit easy insertion and removal of the titration cell P from the bottom.

A removable holder M was fixed to the bottom plate N so that the titration vessel was always correctly positioned in the light path, and did not slide off if the bottom plate were tilted while removing or inserting it. A device O under spring-tension was fixed to cylinder A and designed so that a metal rod rotated under and supported the bottom plate N during a titration. At the end of a titration the knob on device O was turned with one hand and the bottom plate N with holder M and titration vessel P removed with the other hand.

References p. 463

The sample holder M used in the reported experimental work was for 200 ml tall form beakers, but other holders can be substituted on the bottom plate N for larger or smaller beakers. Two holes were cut in the sides of cylinder A diametrically opposite each other for entrance and exit of the light beam.

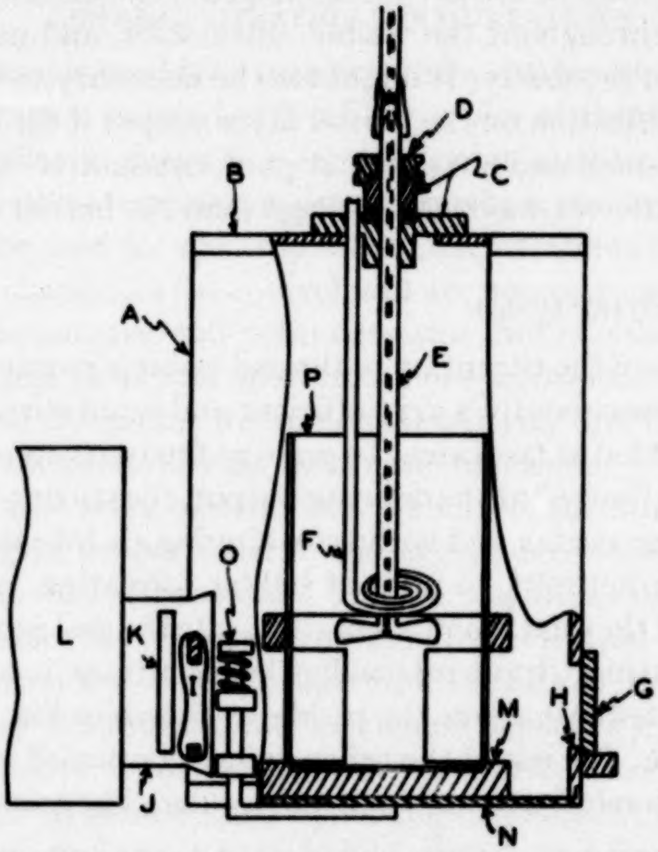

Fig. 2. Partial cut-away diagram of the titration cell compartment.

Light source and filter system

A filter holder J and light source L were mounted on cylinder A so that the light beam passed through the entrance hole I. Various light sources can be readily interchanged. Low intensity radiation from a flashlight bulb and battery is suitable in certain specific titrations, but for general use with many different indicators and solutions a rather high intensity light source powered from a constant line voltage regulator is desirable. For convenience an old-type lamp housing and 6-volt tungsten bulb from a Beckman DU spectrophotometer was used for all of the reported experimental results. In this case a combination 6-volt transformer and line voltage regulator was used with the light source. No optics were used to focus the light beam on the detector because sufficient focusing was obtained from the curved walls of the titration beaker.

Various interference and colored glass filters covering the visible range and also down to 350 millimicrons were used to isolate narrow bands of radiation characteristic of the indicator absorption bands. For certain specific titrations filters would not be necessary, but they were used to provide high sensitivity for operation of the derivative unit. An interference wedge or filter wheel should be more convenient than the filter holder used.

Light detector

An inexpensive barrier layer cell, International Rectifier Corporation's Model B 2 M "Sun battery", was used for all reported experimental results, and it was attached directly to cylinder A at hole H with a light-tight seal. This detector has a relative sensitivity curve quite similar to the eye and it is quite insensitive on the blue and red ends of the visible spectrum. However, it was suitable for all titrations attempted and was used for one specific titration in the region of 350 millimicrons.

Light detector units may be readily interchanged if the need arises. A light detector with high sensitivity throughout the visible, ultraviolet, and near infrared would be desirable for maximum flexibility. It might also be necessary to have a more sensitive detector or some amplification on the barrier layer output if the absorbance change at the end-point is quite small and not sharp. A photoconductive detector would provide high sensitivity in a different wavelength range than the barrier layer cell.

Titrant delivery and stirring system

Continuous addition of the titrant up to the end-point is required with the derivative control system, and consequently a very efficient and rapid stirring system is required if the titrant is to be added at fast rates. To prevent fluctuations of solution path length which cause unwanted "noise" at the detector output, the stirring must be accomplished without forming a large vortex and without whipping air into the solution.

MALMSTADT AND ROBERTS[1,4], to prevent bubble formation, used a platinum gauze electrode which served the dual functions of stirring baffle and generator electrode when electrolytically generating titrant internally. When titrant is added from a buret, a teflon spiral F suspended just above the paddle as shown in Fig. 2 is a good substitute for the platinum gauze. The use of the teflon spiral eliminated vortices and permitted fast stirring rates with relatively large stirrer paddles. The spiral was cut from 1/16" teflon sheet.

Generally, when titrant is added from a buret for automatic derivative potentiometric and spectrophotometric titrations[1,2], rapid delivery and efficient mixing of titrant are made possible by careful adjustment of the delivery tip just above the paddle and against the stirrer shaft. In order to eliminate the delivery tip and to provide a simple method of adjusting titrant flow rate, a new delivery system was investigated whereby the titrant flows through a capillary stirring shaft and out a small hole near the paddle. The method provided excellent mixing and permitted fast addition of titrant.

When the titrant reaches the paddle it can flow in many directions depending where the final orifice is made and the design of the stirrer paddles. The best mixing efficiency was obtained when the orifice was placed directly between the paddles and titrant was allowed to flow in a direction perpendicular to the stirrer shaft. Paddles which exert a lifting effect were used. Capillary stirrers of various lengths and bores can be constructed in order to obtain various flow rates of titrant.

Derivative control unit

No changes were made in the commercially available Sargent-Malmstadt control unit[3,6]. A reversing switch was connected to the output terminals of the light detector so that the positive voltage swing required for proper operation of the commercial control unit was applied to the input at the end-point. The switch was put in the "+" position if the intensity of radiation incident on the detector increased at the end-point, corresponding to a decrease of absorbance at the preselected wavelength. It was put in "—" position if the incident radiation on the detector decreased at the end-point, corresponding to an increase of absorbance. Therefore, with the switch in the correct position, a positive voltage was applied to the grid of the input tube whether the solution absorbance increased or decreased.

GENERAL TITRATION CONSIDERATIONS

When a color indicator is used for a titration and a characteristic absorption band for one form of the indicator is isolated with a filter, a plot of absorbance *versus* milliliters of titrant is quite similar in shape to a sigmoid potentiometric curve. Therefore, the second derivative end-point termination procedure which can be used for potentiometric titrations[2,7] can also be used for spectrophotometric titrations by using the color indicator procedures. No changes in the control unit are necessary in changing from potentiometric to spectrophotometric end-point detection, but in either case the input signal must be sufficiently large for proper operation. For spectrophotometric detection there are several factors that determine instrument sensitivity and these can be important when adapting a specific procedure for automatic titrations.

The automatic titrator relay system, which controls the buret valve, requires for proper operation a signal proportional to the second derivative of the light detector output and of a certain minimum voltage, and the magnitude of the second derivative signal is larger the greater the rate of change of detector output voltage. Therefore, all instrumental and solution factors which determine the rate of change of detector output voltage are effective in determining the instrument sensitivity.

The relative sensitivities of the tungsten source and detector and transmittance of the titration vessel are all wavelength dependent. Consequently, the detector output is greatly dependent on the wavelength band isolated, and this is determined by the specific indicator used. Most of the visual color indicators have large absorption bands in the region of 500-600 millimicrons, which is the region of very high sensitivity for the combination of tungsten light source, glass beaker and barrier layer detector. Therefore, with this given instrumental combination, a given rate of change of absorbed radiation can give a relatively large rate of change for the detector output voltage in the region of 500-600 millimicrons, and a relatively small rate of change at much shorter or longer wavelengths. The various spectrophotometric instrumental components can be changed to produce high sensitivity in selected wavelength regions, but no combination is suitable for all possible regions. However, the chosen combination of components is suitable for automation of most well known visual color indicator titration procedures, as demonstrated by the experimental results.

When the sensitivity of the instrumental combination is very low for a selected wavelength band, the solution factors become more important in determining whether or not the rate of change for the detector output is sufficient for operation of the control unit. If the output of a barrier layer detector operates into a high impedance, such as the derivative control unit, the detector output voltage is approximately proportional to the solution absorbance, and the rate of change for the detector output is proportional to the rate of change for the absorbance; a consideration of the absorption law shows that the rate of change for absorbance is proportional to the solution path length, indicator absorptivity, and the rate of change of indicator concentration.

For general titration purposes the path length is not conveniently changed over significant limits. The absorptivity is a function of wavelength and is often greatly affected by the wavelength of the radiation used. The rate of change of indicator concentration depends on several factors, including the rate of titrant addition, rate of mixing, rate of reaction between the substance to be determined and the titrant, and the rate of the indicator reaction.

Ideally, the rates of mixing, titration reaction, and indicator reaction should be infinitely fast so that the titrant could be introduced at maximum delivery rate of the buret. Although these rates are not infinitely fast, all of the rates are sufficiently rapid for most of the commonly used titration procedures to be made automatic with the derivative spectrophotometric system.

The titrant addition and mixing system is very efficient and provides almost instantaneous mixing at titrant flow rates as high as 10-15 milliliters per minute, and it is not a serious limitation for rapid automatic derivative titrations. There are many titration procedures where the titration and indicator reactions are so rapid that the mixing rate determines the titrant delivery rate, and rates of 10-15 ml/min are possible without any blank corrections and faster rates if blank corrections are used. There are also many titration methods where either the rate of titration reaction or indicator reaction or both limit the titrant delivery rate, and on the basis of experimental results, the optimum titrant delivery rate is usually between 3-10 ml/min.

If both instrumental and solution factors for a specific titration provide a very small rate of change for detector output voltage which is insufficient to drive the control unit, it is generally possible to change one or more factors to yield an adequate signal. Too high a sensitivity is not desirable because of the possibility of interference from detector output "noise" and overdriving the control unit. However, there is little or no danger of too high a sensitivity with the relatively low sensitivity detectors such as the barrier layer cells.

There are several methods by which the best filters for maximum sensitivity can be determined. When visual color indicators are used, satisfactory filters can often be determined from a knowledge of the wavelengths for the complementary colors of the indicator forms and the spectral sensitivities of the components on the spectrophotometric attachment. Another method is to determine the best filter under actual working conditions for a specific titration and indicator. Each of the available filters within a reasonable wavelength range is inserted and tested separately while performing the specific titration. The titration curve is recorded in each case and the filter providing the best rate of change of detector output is chosen as the most suitable under the given working conditions.

EXPERIMENTAL RESULTS

Several typical acid-base and oxidation-reduction titrations were performed and the significant characteristics of the specific indicators for use in the automatic derivative titrator are discussed in connection with the titrations for which they were used. For each indicator a filter was chosen that provided optimum instrument sensitivity, and the results are summarized in Table I. Interference filters with about 25 millimicrons bandpass and 20-30% transmission were used in most cases.

Titration procedure

The sample was prepared in a 200 ml tall form beaker and the volume adjusted to about 150 ml or more with the solvent. The beaker was inserted into the sample holder mounted on the bottom plate of the titration vessel compartment, and the assembly was raised into the compartment and held securely in position by rotating the support arm under the bottom plate. A self-zeroing 25 ml buret was filled from a carboy of a specific standard titrant.

A filter characteristic of the indicator absorption band was placed in the filter holder, and the reversing switch at the detector output was put in either the "+" or "—" position depending on whether the radiation incident on the detector increased or decreased at the end-point. The start button on the control unit was pushed to start both the stirring and the flow of titrant, and the titration was automatically terminated at the end-point. The result was read from the buret.

Titration of strong acids with a strong base

Three indicators in the pH range 6-8 were used for titrating 10 ml aliquots of 0.1*N* hydrochloric acid with 0.1*N* sodium hydroxide. Conventional quantities of the usual 0.1% bromthymol blue, phenol red, and chlorphenol red indicators were used for the hydrochloric acid titrations. Ten titrations were automatically performed with each indicator, and the standard deviation for each group of ten was slightly less than 0.02 ml, approximately the reading error of the buret. The maximum deviation of the averages of the three groups was 0.02 ml.

All reaction rates were sufficiently rapid so that at delivery rates of about 5-10 ml/min all of the titrations were automatically terminated at their equivalence points; at delivery rates of 10-15 ml/min there was a small but reproducible blank in each case.

Titration of weak acids with a strong base

Ten 10 ml aliquots of a 0.1*N* potassium acid phthalate solution were automatically titrated with 0.1*N* sodium hydroxide for each of three different indicators, thymol blue, cresol red, and phenolphthalein. The titrations were all automatically terminated very close to their equivalence points, and the standard deviation for each group was 0.03 ml or less. Titrant delivery rates similar to the hydrochloric acid-sodium hydroxide titrations were possible when using thymol blue and cresol red indicators. However, the reaction rate of phenolphthalein from the basic to acid form was relatively slow and caused streaming of colored indicator into the light path somewhat prior to the equivalence point if the titrant delivery rate was much faster than 5 ml/min. At 5 ml/min or less the results with phenolphthalein were very good and the end-points were coincident with their equivalence points. This example illustrates that if an indicator reaction rate is the limiting factor for titrant delivery rate, it might be possible to use one or more other indicators.

Ten 20 ml aliquots of acetic acid were also automatically titrated with 0.1*N* sodium hydroxide for each of three indicators, thymolphthalein, phenolphthalein, and thymol blue, and the standard deviation of each group was within the reading error of the buret and the range of the three average results was 0.02 ml. The titrant delivery rates with both phenolphthalein and thymolphthalein indicators were limited to 5 ml/min, but faster delivery rates were possible with thymol blue indicator.

Titration of weak and strong acid mixtures with strong base

Aliquots of two different mixtures of perchloric and acetic acids were pipetted into the titration beakers and diluted to about 150 ml with acetone and water, providing a starting solution containing about 80% acetone. The acetone media resulted in sharp end-points for the successive titration of both the perchloric and acetic acids. Indicators for each of the two end-points were added at the start of the titration and after the automatic termination of the perchloric acid end-point, the buret was read and the start button was pushed again to start the flow of titrant which was then automatically terminated at the acetic acid end-point.

0.3 ml of bromphenol blue and 0.7 ml of cresol red were added as the indicators for the first and second end-points, respectively. Both of these indicators absorb in the region of 575 millimicrons and correspond to an absorbance increase at their end-points. Therefore, no changes in filter or reversing switch position were necessary in proceeding from the first to second end-points.

One acid mixture contained equal amounts of the acids and the other contained five parts of perchloric to one part of acetic acid. The standard deviation for both end-points in both mixtures was within the buret reading error. The only titrant delivery rate used was 7 ml/min, and at this rate the automatically obtained end-points corresponded to their equivalence points, within 0.1% relative for the first and 0.2% relative for the second.

The successive titration of phosphoric acid to the first and second end-points with 0.1*N* sodium hydroxide was also automatically performed in the derivative spectrophotometric titrator using methyl red indicator for the first end-point and a mixed indicator of thymolphtalein and phenolphthalein for the second end-point. Both indicators undergo sharp absorbance changes in the wavelength region of 550 millimicrons, and it was not necessary to change filters in proceeding from the first to the second end-point, but it was necessary to flip the detector output reversing switch from "+" to "—" after the first end-point because methyl red decreased in absorbance at the first end-point and the mixed indicator increased in absorbance at the second end-point. Therefore, after automatic termination at the first end-point, the buret was read, the reversing switch changed to

References p. 463

the "—" position, and the start button on the control unit pushed to again start the flow of titrant, which was automatically terminated at the second end-point.

Five 10 ml aliquots of 0.1*M* phosphoric acid were titrated with 0.1*N* sodium hydroxide, and the standard deviation for the first end-point was 0.02 ml and the second 0.07 ml. There was a difference of 0.04 ml between the averages of the start-to-first and the first-to-second end-point results. The titrant delivery rate was limited to about 5 ml/min because of the slow reaction rate of the mixed indicator.

Titration of ammonia-boric acid solution with hydrochloric acid

Five 25 ml aliquots of an ammonia-boric acid solution, quite similar in concentration to those obtained from a Kjeldahl distillation, were automatically titrated and required an average of 21.68 ml of 0.1*N* hydrochloric acid to reach the bromcresol green end-point. The standard deviation of the five results was 0.02 ml and the end-points were coincident with the equivalence points for the only titrant delivery used of about 7 ml/min.

Titration of ferrous, arsenite and hydroquinone solutions with Ce(IV)

Standard procedures were used to prepare ferrous, arsenite, and hydroquinone solutions for automatic titration with standard 0.1*N* Ce(IV) solution. Several 10 ml aliquots of each were automatically titrated and the standard deviation in all cases was 0.02 ml, about the buret reading error, and all were terminated at their equivalence points. The relatively slow reaction rate for the ferroin indicator limited the titrant delivery rate to about 3-5 ml/min. The filters used and indicator concentrations are tabulated in Table I along with the same data for all of the reported titrations.

TABLE I

OUTLINE OF USEFUL INFORMATION FOR VARIOUS AUTOMATIC DERIVATIVE SPECTROPHOTOMETRIC TITRATIONS

Titration	*Indicator*[a]	*Ind. Conc.*[b] *ml*	*Filter* *mμ*	*Switch*[c]
HCl with NaOH	Bromthymol blue	0.1	600	—
HCl with NaOH	Phenol red	0.1	550	—
HCl with NaOH	Chlorphenol red	0.1	575	—
KH phthalate with NaOH	Cresol red	0.1	550	—
KH phthalate with NaOH	Phenolphthalein	0.5	550	—
KH phthalate with NaOH	Thymol blue	0.2	575	—
Acetic acid with NaOH	Thymol blue	0.2	575	—
Acetic acid with NaOH	Phenolphthalein	0.5	550	—
Acetic acid with NaOH	Thymolphthalein	0.5	575	—
$HClO_4$ and acetic acid with NaOH	Bromphenol blue	0.3	575	—
$HClO_4$ and acetic acid with NaOH	Cresol red	0.7	575	—
H_3PO_4 and $H_2PO_4^-$ with NaOH	Methyl red	0.15	550	+
H_3PO_4 and $H_2PO_4^-$ with NaOH	Mixed indicator[d]	0.35	550	—
NH_3-boric acid soln. with NaOH	Bromcresol green	0.3	550	+
Fe(II) with Ce(IV)	Ferroin[f] (0.25*M*)	0.1	525	+
Ce(IV) with Fe(II)	Ferroin[f] (0.25*M*)	0.1	525	—
AsO_2^- with Ce(IV)[e]	Ferroin[f] (0.25*M*)	0.1	525	+
Hydroquinone with Ce(IV)	Ferroin[f] (0.25*M*)	0.1	525	+
$S_2O_3^{-2}$ with I_2	Amylose starch	1.0	600	—
I_2 with $S_2O_3^{-2}$	None	None	350 to 370	+

[a] All indicators were 0.1% solutions unless otherwise specified.

[b] Indicator concentration given as milliliters added per 150 milliliters of solution.

[c] Reversing switch position at detector output.

[d] Equal mixture of thymolphthalein and phenolphthalein.

[e] 1.5 ml of 0.1% osmic catalyst was added and the titration run at about 40°C.

[f] Ferrous *o*-phenanthroline complex.

Titration of Ce(IV) with ferrous iron solution

Automatic titrations of several 10 ml aliquots of 0.1 *N* Ce(IV) with 0.1 *N* ferrous iron were performed and results similar to the above titrations were obtained. The method was also applied to the determination of oxalate by oxidizing the oxalate with excess standard Ce(IV) in the presence of iodine monochloride catalyst at 50-60°C for 5 minutes. The excess Ce(IV) was then automatically back titrated with the 0.1 *N* ferrous solution, giving the same excellent results as for the other methods.

Titration of thiosulfate with iodine

The titration of thiosulfate was performed using conventional solution preparation, 0.01 *N* iodine as titrant, and an amylose starch solution as indicator (available from G. F. Smith Chemical Co.). Ordinary starch solution was not satisfactory as an indicator because of its very slow reaction. The precision of the automatic results for several thiosulfate titrations was equivalent to that for the previously described methods at titrant delivery rates up to about 7 ml/min. In order to maintain a standard iodine solution, however, it would be necessary to eliminate the gum rubber tubing used for the buret valve and replace it with an automatic stopcock closure device.

Titration of iodine with thiosulfate

The addition of starch indicator at the beginning for a titration of iodine with standard thiosulfate did not provide a sharp absorbance change in the region of the equivalence point, and consequently the starch was not a suitable indicator for this specific automatic titration. However, it was possible to perform this titration precisely and accurately without an added indicator by using the strong absorption band of iodine itself in the ultraviolet region. The transmission of the glass beakers and the sensitivities of the barrier layer cell and tungsten source were sufficient to provide an adequate signal for operation of the control unit when a narrow band of radiation was isolated at about 350 to 370 millimicrons.

The use of iodine as its own indicator and application of the automatic second derivative technique to the resulting titration curve is another example of a general type of spectrophotometric titration which was described by MALMSTADT AND ROBERTS[1,4] and used by them for the automatic titration of iron[4] and titanium[5].

Several aliquots of 0.1 *N* iodine solution were automatically titrated with 0.1 *N* thiosulfate without any added indicator and the results were both precise and accurate, within the reading error of the buret. The titrations were terminated at their equivalence points for delivery rates of about 5 ml/min; at delivery rates of 10-15 ml/min small but very reproducible blanks were obtained.

SUMMARY

A convenient and compact automatic derivative spectrophotometric titrator is described which is suitable for automatically performing a wide variety of the well known color indicator titrations without any procedure modifications and usually with few, if any, pretitration considerations and instrument adjustments. The results for many acid-base and oxidation-reduction titrations are presented to illustrate the general applicability and important characteristics of the instrument.

RÉSUMÉ

Un appareil est décrit permettant d'effectuer automatiquement un grand nombre de titrages bien connus, utilisant des indicateurs colorés, sans aucune modification du procédé. Les résultats de plusieurs titrages alcali-acidimétriques et d'oxydo-réduction sont présentés pour illustrer les nombreuses applications et les caractéristiques importantes de cet appareil.

ZUSAMMENFASSUNG

Ein Titrimeter wird beschrieben, welcher die automatische Ausführung einer grossen Zahl bekannter Titrationen mit farbigen Indikatoren ohne Änderung des Verfahrens erlaubt. Die Ergebnisse von vielen Säure-Base- und Oxydo-Reduktions-Titrationen werden mitgeteilt um die allgemeine Anwendbarkeit und die wichtigsten Eigenschaften des Apparates zu belichten.

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THE *IN SITU* DETERMINATION OF IRON AND OF COPPER IN WINE

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INTRODUCTION

The determination of iron in wine is a requisite routine plant control analysis. A wine processing procedure which leaves the bottled wine free from iron in excess of 5-10 parts per million is followed. Bottled wine having iron in excess of this limit promotes "iron casse" (turbidity due to formation of insoluble hydrolytic iron compounds). Such conditions downgrade wine in quality and in resultant consumer acceptance.

The determination of copper in wine is of greater significance. Copper content in excess of 1-2 parts per million contributes to the development of "off flavors" during short periods of shelf life. In the case of dairy products (such as milk and butter) this quality impairment is termed "a tallowy flavor".

Procedures for the determination of iron in wine, at present preferred, involve "wet ashing" in the preparation of the sample for analysis. All organic matter of the wine sample should be oxidized and removed by this process. Two reaction techniques have been commonly applied in this preparational procedure. First, the nitric-perchloric acid digestion. Second, the hydrogen peroxide oxidation.

The present work has for its objective the development of a procedure for the determination of iron and of copper in wine without requisite wet ashing accompanying procedure in the preparation of the sample for analysis. This *in situ* procedure is thus more direct, time saving with procedural simplification, with no loss of specificity and with much increased sensitivity. The accuracy thus attained is, as will be experimentally demonstrated, comparable to the former procedures involving wet oxidation and spectrophotometrical metal contaminant evaluation.

PREVIOUS STUDIES

Early published work in the determination of iron in wine was by SAYWELL and associates[1]. This work involved techniques in the improvement of the procedures described by LEAVEL AND ELLIS[2]. The latter employed mercaptoacetic acid in the colorimetric determination of iron after a somewhat tedious sample preparation. These new procedures are reviewed in detail in the book ***Phenanthroline and Substituted Phenanthroline Indicators***[3].

The latest published work on the use of 1,10-phenanthroline in the determination of iron in wine is by DEIBNER AND BOUZIGUES[4]. These authors fail to refer to the work of

SAYWELL and associates[1,2,3], and include a wet ashing procedure employing hydrogen peroxide. This procedure is more time-consuming and less effective than nitric-perchloric acid wet oxidation[5,6].

The two substituted 1,10-phenanthrolines employed in the present method were described by SMITH, MCCURDY AND DIEHL[7], and by SMITH AND WILKINS[8]. They are commercially available under the trade names "Bathophenanthroline" (4,7-diphenyl-1,10-phenanthroline) and "Bathocuproine" (4,7-diphenyl-2,9-dimethyl-1,10-phenanthroline). The former is specific for the spectrophotometric determination of iron in the presence of copper. The latter is specific for the spectrophotometric determination of copper in the presence of iron. Both these reagents having the methine chromophore functional group are outstanding in the form of their iron(II) and copper(I) complex cations. They have the advantage of being highly specific, high in sensitivity, extractable using immiscible organic solvents, and free from narrow limits of pH environment with color stability over long periods in contact with atmospheric oxygen. This combination of qualities makes practical the *in situ* determination of both iron and copper in wine. The elimination of the otherwise prerequisite wet ashing of the wine sample provides a major simplification of operational procedures without loss in accuracy.

SAMPLES FOR ANALYSIS

The samples for analysis were all of Continental European vintage, three white wines and two red wines. The various wine samples are listed in Table I.

TABLE I

WINE SAMPLE IDENTIFICATION AND TYPE

Sample no.	*Type*	*Trade name*	*Winery*	*Origin*	*Alcohol content vol. %*	*Wt. of 5 ml sample g*
1	Red	Famosa Sherry	Manual Fernandez	Spain	19.5	4.984
2	White	Graacher Muenzlay (1949)	Max Huesgen	Germany	11.5	4.972
3	White	Sauternes (1952)	Lolivier Frères	France	13.0	5.027
4	Red	Moulin-A-Vent (1952)	F. Hasenklever	France	12.0	4.926
5	White	Binger-Babbel-Lieschen (1952)	Heinrich Jung	Germany	10.5	4.982

The samples of wine listed in Table I were purchased from the Great Lakes Wine Company of Chicago, Illinois (Permit No. 9-1-87), importers.

PERTINENT REFERENCE PHYSICAL CONSTANTS OF WINE SAMPLES

Data relative to the pH of the various wine samples as sampled, and after buffer solution was added, together with the weight of a pipetted 5 ml sample are given in Table II.

Reagents required

Perchloric acid. Double distilled 70-72% is preferred. Single vacuum distilled acid may be employed.

Nitric, sulfuric and hydrochloric acids. Reagent grade acids (67%, 95% and 37% strength respectively).

Water. The best sample of de-ionized water should be employed and for a series of determinations a large enough supply should be at hand to insure comparable blank corrections.

TABLE II

PHYSICAL CONSTANTS OF WINE SAMPLES
(ORIGINAL pH, BUFFERED pH AND SAMPLE WEIGHT)

Wine sample no.	*Sample pH*	*Sample buffered in equal volumes. Buffer pH = 4.0*	*Sample buffered in equal volumes. Buffer pH = 7.1*	*Wt. of 5.00 ml sample g*
1	3.5	4.3	5.9	4.984
2	3.1	4.1	5.7	4.972
3	3.6	4.1	5.7	5.027
4	3.4	4.0	5.7	4.926
5	3.5	4.0	5.7	4.982

Buffer solutions. For pH 4.0 an acetic acid-sodium acetate buffer is employed. For the buffer (pH 7.1), an ammonium acetate buffer is suitable.

Ethyl alcohol. Reagent 95% ethanol.

Copper sulfate solution. A solution standardized to contain 0.1277 mg of copper per gram of solution. Weight burets were employed in sampling this solution. Other values may be employed of comparable concentration.

Isoamyl alcohol. Reagent grade redistilled.

Hydroxylamine hydrochloride. Best reagent grades tested to prove their limited amount of iron impurities which seem always to be present to a greater or less degree. Both 10% and 20% by weight aqueous solutions are prepared.

1,10-Phenanthroline, aqueous solution. Mol. wt. = 198 as the monohydrate. Prepare a 0.01 *M* solution in de-ionized water.

Bathophenanthroline (4,7-diphenyl-1,10-phenanthroline). Mol. wt. = 332. Prepare a 0.01 *M* solution in ethyl alcohol.

Bathocuproine (4,7-diphenyl-2,9-dimethyl-1,10-phenanthroline). Mol. wt. = 360. Prepare a 0.01 *M* solution in ethyl alcohol.

Apparatus required

For wet ashing procedure it is always preferable to employ Vycor digestion flasks. The perchloric acid-water azeotrope has a boiling point of approximately 203°C at atmospheric pressure. Rapid cooling of pyrex flasks from this temperature to 15 or 20°C sometimes may cause too great heat strain and result in fractured flasks. It is not a requisite to employ Vycor reaction flasks; however, it is not only a wise precaution but makes possible chilling of such flasks from 200°C by immersion at once under running cold tap water or preferably by immersion in a bath of ice-water with swirling motion for rapid cooling.

Transfer pipets are suitable for the sampling of the wine for analysis as well as for the addition of reagents during the progress of the reactions. Individual pipets used exclusively for separate reagents should be provided.

Weight burets should be employed for the addition of standard copper sulfate solution in the determination of the blank as well as the wine copper plus blank determination.

The stock units represented by the standard type of 60 ml separatory funnel are less convenient in application because of the diameter of the opening just above the delivery stopcock. Using pyrex separatory funnels it is preferred to remove the stock stopcock immediately above its union with the bowl of the apparatus and to attach in its place a micro-stopcock having a 0.5 mm bore, a two cm wide barrel and 3 mm bore side terminals. A group of such modified separatory funnels with supporting rack are much to be desired. A photo reproduction is shown in Fig. 1.

The wet ashing apparatus assembly[5] is recommended and precludes the use of a fume hood which is a worthwhile inovation. A fume hood may be employed in its stead but the refluxing still head is still requisite.

The process may be carried out as described employing a Carey Model 11 recording instrument in place of the Beckman U.V. apparatus.

CONTROL ANALYTICAL PROCEDURE IN THE REFERENCE ANALYSES FOR COPPER AND IRON IN WINE

Determination of iron

A modification of the procedure of SAYWELL[1] was used utilizing nitric-perchloric acid wet oxidation and by spectrophotometric estimation of iron using 1,10-phenanthroline as color producing ligand. The Saywell procedure was modified only in the use of 5 ml of wine in place of a 1-2 ml sample. In addition the ferroine reaction complex of iron(II) was determined employing a Beckman D.U. spectrophotometer and a 512 mμ light source. Both these alterations were used in the interest of accuracy. The molecular extinction coefficient applied was 11,500 with cell cuvettes of 1 cm light path. The calculation involves the formulation:

$$\text{optical density} = ECl$$

where (E) is the molecular extinction coefficient, (C) is the concentration of iron in gram atoms per liter and (l) is the light path in cm. By reference to a graph previously prepared relating optical density as abscissa and parts per million of iron as ordinate the calculation may be simplified.

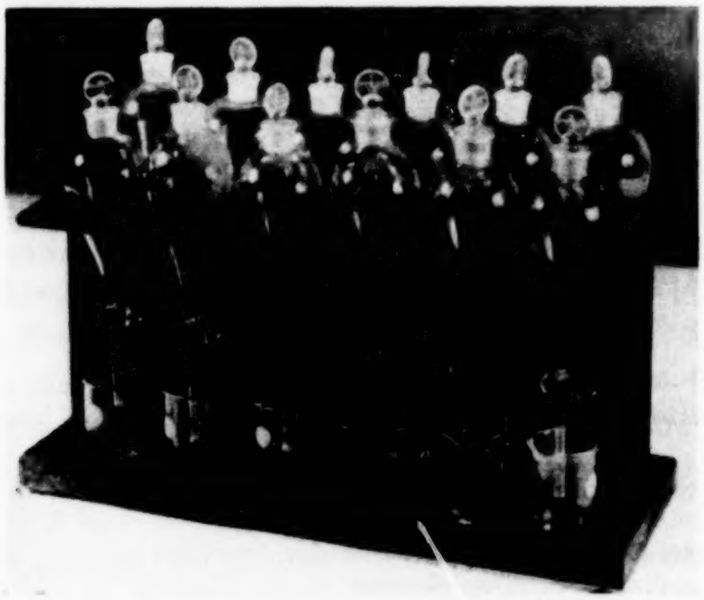

Fig. 1. Modified separatory funnels and rack.

A 5 ml sample of wine is transferred to a 250 ml Vycor Erlenmeyer flask containing 10 ml of reagent nitric acid and 5 ml of 70% perchloric acid. The digestion apparatus employed is that described by one of the authors (GFS)[5], whereby a fume hood is not required. After the initial reaction has subsided, heat is applied from a medium heat electric hot plate, refluxing still head and fume eradicator in place and well vented by use of a water aspirator.

When all nitric acid excess has been expelled and dense fumes of perchloric acid are evolved, discontinue the digestion. Remove the reaction flask and partially cool the contents under a stream of running tap water. Rinse and remove the refluxing still head and transfer the contents of the flask quantitatively to a 100 ml pyrex beaker and add 2 drops of reagent sulfuric acid.

Provide the beaker with a cover glass using twin cover glass hooks. By use of a moderately heated hot plate in a fume hood, evaporate the sample to moist dryness. Dissolve the beaker contents after the addition of 3 drops of reagent hydrochloric acid and 1 ml of water. Add 1 ml of reagent hydroxylamine hydrochloride and warm to insure complete solution and reduction of ferric iron. Buffer the solution by the addition of 5 ml of buffer (pH 4.0). Add 1 ml of 0.01 M aqueous 1,10-phenanthroline solution to form the colored Fe(II) complex. Transfer the solution thus prepared to a 10 ml glass stoppered volumetric flask and dilute to volume with de-ionized water. The spectrophotometric evaluation of iron as above outlined completes the determination. A blank correction is applied using a correction for reagent iron content following the same procedure throughout, without the addition of the wine sample. Water is used as reference for 100% transmission in the spectrophotometric evaluation. (The reference cell in the case of bathophenanthroline and bathocuproine chelation and spectrophotometric determination is one composed of *iso*amyl alcohol and ethyl alcohol in the proportions 6 volumes of the former to 4 volumes of the latter.)

Determination of copper

The blank determinations employed were found to be small but measurable. Because of the very low copper content of the wines it was thought to be preferable to add copper to the sample for analysis. This seeding technique is often used in gravimetric[9] and radiochemical processes and serves as a check on the accuracy of the method and the reliability of the results.

The wet ashing procedure just previously described in the determination of iron is followed in its entirety up to the point at which the evaporated solution of the wet ashing residue is moist-dry and free from excess perchloric acid. The remainder of the procedure in the determination of copper is as follows:

Take up the moist-dry beaker contents by the addition of 3 drops of reagent hydrochloric acid and 2 ml of water. Heat gently to promote complete solution and transfer the dissolved contents of the beaker quantitatively to a 60 ml glass stoppered separatory funnel. Add 5 ml of buffer solution (pH 7.1), and a weighed amount of copper sulfate solution, 2 ml of 10% hydroxylamine hydrochloride solution and 2 ml of 0.005*M* bathocuproine. If not at this point a total of approximately 20 ml in volume, add water to this total volume. Add 6 ml of *iso*amyl alcohol.

Shake the stoppered flask contents 60 seconds and then allow the two liquid phases to separate during 5 minutes. Draw off the lower aqueous layer and transfer the alcohol layer quantitatively into a 10 ml volumetric flask and dilute to the mark by use of ethyl alcohol. Determine the absorbancy employing a Beckman D.U. spectrophotometer set at 479 mμ light source. A blank determination on reagents completes the procedure. The molecular extinction coefficient applied is 14,200.

THE *in situ* DETERMINATION OF IRON BY DIRECT COLOR FORMATION AND IMMISCIBLE SOLVENT EXTRACTION AFTER BATHOPHENANTHROLINE CHELATION

Determination of iron in red wines

The wine sample reaction reagents are as follows (use a 100 ml beaker in sampling and preliminary reactions):

5.00 ml of wine. (Three ml may be used for iron content in excess of 10 p.p.m.)
5.0 ml of buffer solution (pH 4)
2.0 ml of 10% aqueous hydroxylamine hydrochloride
1.0 ml of 0.01*M* bathophenanthroline solution
2.0 ml of 95% ethanol.

The reaction mixture is now approximately 25% ethanol by volume. Heat the contents of the beaker to a gentle boil and boil for one minute. Transfer the contents of the beaker while still hot to a 60 ml glass stoppered separatory funnel. Add 6 ml of *iso*amyl alcohol and shake during 30 seconds. Allow the two liquid phases to separate for 3 minutes and draw off the lower aqueous layer. The beaker used for the pre-digestion is now rinsed with 1 ml of 95% ethanol, and 2-5 ml portions of water, transferring the rinsings to the separatory funnel containing the alcoholic extract of the reaction mixture. Add 10 ml of buffer solution (pH 4.0), and shake the contents of the separatory funnel 30 seconds. Allow the two liquid phases to separate 5 minutes and draw off the lower aqueous layer. The alcohol phase is transferred quantitatively to a 10 ml graduated flask and diluted to the mark with 95% ethanol.

The absorbancy is measured as previously described employing a light source of wave-length 533 mμ. The molecular extinction coefficient used in the calculation was 22,400. A blank correction to correct for contamination of reagents is applied as before.

Determination of iron in white wines

For this procedure the reagents employed are the same as those listed for the red wine procedure with added 2 ml of ethanol omitted.

The wine sample and reagents in a 100 ml beaker are heated gently to boiling and boiled for 60 seconds. The beaker contents are allowed to cool. Transfer the beaker contents into a 60 ml separatory funnel rinsing the beaker first with 1 ml of 95% ethanol and 2-5 ml portions of water. Add 6 ml of *iso*amyl alcohol. Shake the flask for 2 min to establish equilibrium and allow the two liquid phases to separate 5 min. The aqueous layer is then drawn off and the alcohol layer transferred to a 10 ml graduated flask and diluted to the mark with 95% ethanol. Determine the absorbancy as before at 533 mμ light source and calculate the iron using 22,400 for the molecular extinction coefficient. Again apply a reagent blank correction.

THE *in situ* DETERMINATION OF COPPER BY DIRECT COLOR FORMATION AND IMMISCIBLE SOLVENT EXTRACTION AFTER BATHOCUPROINE CHELATION

Determination of copper in red and white wines

The wine sample reaction ingredients are placed in a 60 ml glass stoppered separatory funnel in the order given below:

5.00 ml of wine
5.0 ml of buffer (pH 4.0)
0.2 ml of standard $CuSO_4$ solution (wt. buret sampling)
2.0 ml of 10% hydroxylamine hydrochloride solution
2.0 ml of bathocuproine solution

The contents of the separatory funnel are shaken for 2 min and the two liquid phases are allowed to separate. The aqueous layer is then drawn off. Add 5 ml of buffer (pH 7.1), and 5 ml of water. Again shake for 1 min and allow 5 min for phase separation. The aqueous layer is again drawn off and the alcohol layer transferred quantitatively to a 10 ml volumetric flask and diluted to volume with 95% ethanol. Absorbancy is then determined using a light source of 479 mμ. The calculation is again made employing 14,200 as the molecular extinction coefficient. A blank determination is made to correct for reagent contamination.

For the highest possible accuracy in the *in situ* determination of iron and copper the solution used as reference for 100% transmission should be prepared as follows: Extract an analysis size sample of the wine with 6 ml *iso*amyl alcohol. Draw off the lower phase. Transfer the alcohol layer to a 10 ml volumetric flask and dilute to volume with 95% ethanol. Spectrophotometric standardization using this solution compensates for any extracted color not due to the Fe(II) or Cu(I) complex of the reacting ligand.

The spectrophotometric reference solution just described was used in obtaining the results shown in Tables IV and V. If the above described spectrophotometric reference solution was not used, the determination of iron and copper was in error by approximately 1% for all the wines analyzed. The Red Burgundy wine was an exception. Failure to use the compensating spectrophotometric reference solution would lead to errors of approximately 5% total for both iron and copper.

The results in the determination of iron and of copper in wine sample number four (red wine), are given in Tables III and IV for the purpose of illustrating multiple duplicate analyses and variation in results of individual replicas of the same sample.

TABLE III

DUPLICATE DETERMINATION OF IRON IN SAMPLE NUMBER FOUR, FRENCH VINTAGE RED WINE

Wet ashing procedure 1,10-phenanthroline chelation			*Direct extraction 4,7-diphenyl-1,10-phenanthroline chelation*		
Sample wt. g	*Absorbancy = 512 mμ (blank corrected)*	*Fe found p.p.m.*	*Sample wt. g*	*Absorbancy = 533 mμ (blank corrected)*	*Fe found p.p.m.*
4.93	0.807	8.33	2.96	0.973	8.19
4.93	0.808	8.16	2.96	0.983	8.28
4.93	0.833	8.20	2.96	0.993	8.37
2.96	0.505	8.28	2.96	0.970	8.18
2.96	0.497	8.15	2.96	0.979	8.25
		Av. 8.22			Av. 8.25

From examination of the data of Table III it will be found that the results in the two general procedures, the one with wet ashing of the wine sample for analysis, compared with the newly described procedure of *in situ* determination, are directly comparable in accuracy. The range of determined values in each case is 0.18 p.p.m., 0.19 p.p.m., respectively, and the average deviation is similarly comparable at 0.064 p.p.m. and 0.058 p.p.m., approximately 2 parts per hundred of the total iron found.

TABLE IV

DUPLICATE DETERMINATIONS OF COPPER IN SAMPLE NUMBER FOUR, FRENCH VINTAGE RED WINE 4,7-DIPHENYL-2,9-DIMETHYL-1,10-PHENANTHROLINE (BATHOCUPROINE) CHELATION

Wet ashing procedure					*Direct extraction*				
Sample wt. *g*	*Copper added* *µg*	*Copper found* *µg*	*Copper of sample* *µg*	*Copper of sample* *p.p.m.*	*Sample* *g*	*Copper added* *µg*	*Copper found* *µg*	*Copper of sample* *µg*	*Copper of sample* *p.p.m.*
2.96	19.44	21.24	1.80	0.61	2.96	17.11	18.95	1.84	0.62
2.96	34.04	36.02	1.98	0.67	2.96	15.81	17.64	1.83	0.62
2.96	35.96	37.86	1.90	0.64	2.96	16.00	17.95	1.95	0.66
					2.96	17.83	19.75	1.92	0.65
					2.96	16.17	17.95	1.78	0.60
				Av. 0.64					Av. 0.63

From examination of the data of Table IV it will be observed that the results in the two general procedures, wet ashing and direct chelation and extraction give comparable results. The range of values is respectively 0.18 and 0.17 micrograms or 0.06 parts per million. The corresponding average deviations are 0.03 p.p.m. and 0.02 p.p.m.

COMPLETE TABULATION OF RESULTS FOR FIVE INDIVIDUAL WINE SAMPLES

In condensed form tabulation the results from the analyses of five wine samples following both the wet ashing procedure and the *in situ* direct chelation, extraction and spectrophotometric evaluation are given in the data of Table V.

COMMENTARY OBSERVATIONS

It is probable that companion 1,10-phenanthroline copper specific organic ligands could be used to replace bathocuproine in the procedure herein described. One such probable substitute is cuproine (2,2′-diquinoline). The substitution of another organic ligand for bathophenanthroline in the iron determination is more restricted since a type which is iron-specific involves a ligand the copper(I) chelation complex of which is colorless at pH 4 and which, in addition, is also soluble in *iso*amyl alcohol used as immiscible solvent extractant. The use of 1,10-phenanthroline is thus inapplicable. For comparable precision in the determination of copper, if cuproine is to be employed, the magnitude of the wine sample treated would of necessity be increased.

The wet ashing procedure in the preparation of the wine samples for analysis as described provides proof that in such procedure no copper is lost by possible volatilization since the same copper found in direct chelation and extraction duplicated that found when wet ashing was employed. This has also been found to be the case in the determination of copper in paper by J. P. BUTLER[10] who has substantiated that in such method, HNO_3-$HClO_4$ wet ashing procedure in preparation of paper and paper pulp for analyses (as well as the use of bathocuproine as color producing ligand), is highly to be desired.

No hazardous reactions were encountered during the study just recorded and the only complication brought about through the use of the wet ashing procedure described is, that a fume hood is required for conducting the evaporations involved.

References p. 472

TABLE V

TABULAR RESULTS IN THE DETERMINATION OF IRON AND OF COPPER IN WINE
(FOR DETAILED INDIVIDUAL DETERMINATONS SEE TABLE III)

	Wet ashing procedure. $HNO_3 + HClO_4$					*In situ chelation and direct extraction*				
Wine sample number	*Number of replicas*	*Iron found p.p.m.*	*Average deviation p.p.m.*	*Copper found p.p.m.*	*Average deviation p.p.m.*	*Number of replicas*	*Iron found p.p.m.*	*Average deviation p.p.m.*	*Copper found p.p.m.*	*Average deviation p.p.m.*
1	5 and 5	3.94	0.038	1.70	0.036	4 and 5	4.00	0.015	1.66	0.016
2	8 and 5	6.03	0.070	2.05	0.003	5 and 5	6.08	0.024	2.03	0.010
3	5 and 5	7.08	0.052	0.76	0.018	5 and 5	6.95	0.040	0.77	0.014
4	5 and 3	8.22	0.064	0.64	0.030	5 and 5	8.25	0.058	0.63	0.020
5	8 and 5	5.01	0.036	1.21	0.024	5 and 4	5.04	0.036	1.20	0.008

CONCLUSIONS

A new procedure in the determination of iron and of copper in wine has been devised. The process may be applied to both red and white wines of 10-20% alcohol content. The procedure does not require the preliminary treatment of the sample to destroy its organic matter by either dry ashing or wet ashing procedures. This time-consuming operation is eliminated by use of a direct treatment of the wine by suitable reactants, namely 4,7-diphenyl-1,10-phenanthroline (bathophenanthroline), and 4,7-diphenyl-2,9-dimethyl-1,10-phenanthroline (bathocuproine). Chelation by the former with ferrous iron results in the formation of the corresponding tris-ligand-ferrous complex cation which may be extracted quantitatively from the wine employing *iso*amyl alcohol. The latter reagent similarly reacts to form a bis-ligand cation with the cuprous ion and may be similarly extracted. The spectrophotometric estimation of both iron and copper is thus provided for. Both chelation reagents are of high molecular absorptivity at wave-lengths of maximum absorption 533 mμ and 479 mμ, the former at 22,400 and the latter at 14,200 value. This high sensitivity is particularly suited to the accurate determination of the low concentration of iron and of copper ordinarily present in wine of commerce, the influence of which upon quality and shelf life is of prime importance. The new method saves time-consuming operations previously required for the same determinations in preliminary treatment without loss in either accuracy or specificity. The new spectrophotometric applications are provided by new organic reagents which are commercially available and few new types of manipulative equipment are required.

SUMMARY

The improved determination of both iron and copper in red and white wines has been developed which avoids the preliminary process of ashing the sample before processing the ash for the actual evaluation of these two troublesome impurities. The new procedure employs bathocuproine and bathophenanthroline as complexing ligands with spectrophotometric determination of the Cu and the Fe *in situ*. The new method is economical in required analysis time, manipulative details and in quantity of sample involved. It has been shown that the new method is comparable in accuracy to previous published procedures, and as control analyses substitute wet ashing technique, the HNO_3-$HClO_4$ destruction of organic matter, was applied.

RÉSUMÉ

Une méthode est proposée pour le dosage du fer et du cuivre dans les vins rouges et les vins blancs, permettant d'éviter la minéralisation préalable de l'échantillon à analyser. Ce nouveau procédé utilise la 4,7-diphényl-2,9-diméthyl-1,10-phénanthroline et la 4,7-diphényl-1,10-phénanthroline pour le dosage spectrophotométrique du cuivre et du fer *in situ*. Cette méthode est avantageuse du point de vue durée du dosage, manipulations et quantité de vin nécessaire; elle est comparable comme précision aux méthodes déjà publiées, utilisant la minéralisation par destruction de la matière organique par le mélange HNO_3-$HClO_4$.

ZUSAMMENFASSUNG

Eine verbesserte Methode zur Bestimmung von Eisen und Kupfer in Rot- und Weissweinen wurde entwickelt welche die Veraschung der Probe vor der eigentlichen Bestimmung vermeidet. Das neue Verfahren verwendet Bathocuproin und Bathophenantrolin zur Komplexierung; Cu und Fe werden spektrophotometrisch *in situ* bestimmt. Die neue Methode ist sparsam in Bezug auf Zeit, Operationen und Grösse der Probe. Sie ist, was die Genauigkeit betrifft, vergleichbar mit früher veröffentlichten Verfahren. Bei den Kontrollanalysen wurden die organische Stoffen mit HNO_3-$HClO_4$ zerstört.

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A NEW REAGENT FOR THE COLORIMETRIC AND SPECTROPHOTOMETRIC DETERMINATION OF PHOSPHORUS, ARSENIC AND GERMANIUM

by

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The formation of the blue colour known as molybdenum blue is the basis of the more important methods for the colorimetric and spectrophotometric determination of phosphorus, arsenic, silicon and germanium. These analytical methods fall into two main categories: (1) those in which an excess of molybdate and a reducing agent are added, (2) an important method, that of Zindazde, in which only one reagent is used, an empirical solution of molybdenum blue.

The aim of this study has been to find a new reagent for this determination that does not require the use of a reducing agent, as is necessary in (1), and in which the reagent is easy to prepare and not difficult to handle. It should be possible to apply the method over a wider range of concentrations and it is desirable for the reagent to have a determinate composition in so far as this affects the valencies of the molybdenum present and the relationship between their concentrations.

PRELIMINARY CONSIDERATIONS

Previous tests had shown that the reagent must contain both Mo(VI) and Mo(V), in agreement with the different formulas given in the literature. Isolated solutions of Mo(VI) or Mo(V) do not produce a blue colour with phosphorus, so the simultaneous presence of both is indispensable.

The problem of obtaining a reagent containing both Mo(VI) and Mo(V) involves two essential points:

1) The reagent must be stable in air

According to the literature, in the presence of 8*N* HCl pentavalent molybdenum is stable in air, as shown by the colour of the solution; in 6-8*N* HCl the solution contains $MoOCl_5^{-2}$ (emerald green colour), while in 2-6*N* it contains MoO^{+3} (reddish brown colour). Only the emerald green solutions are stable in air for practical purposes.

The solution of Mo(V) has been obtained by reduction of Mo(VI) in hydrochloric acid medium with mercury, a very quick method which does not introduce any foreign element into the solution.

2) The reagent must produce a suitable negative blank test

Dilution of cool or hot solutions, in which both Mo(V) and Mo(VI) are present must not bring about the production of molybdenum blue. For this to apply it is necessary to operate in an acid medium, and experience has shown that sulphuric acid is more effective than hydrochloric acid. This factor is also dependent upon the ratio of Mo(VI) to Mo(V).

PROPERTIES OF THE NEW REAGENT

In the first place, the effect of the *ratio Mo(VI) : Mo(V)* on the stability of reagent and its reaction with the phosphorus has been considered; increasing this ratio does increase the sensitivity of the reaction, a ratio of 3 : 2 being the optimum. A still greater ratio results in a positive blank being obtained.

The effect of *acidity* has already been noted in that it increases the stability of the reagent but diminishes its reaction with phosphorus. A reagent 10*N* in sulphuric acid, and 3*N* in hydrochloric acid is proposed. It is stable for more than six months.

In the study of the corresponding *absorption spectra* it is concluded that the composition of the blue complex formed is independent of the quantity of phosphorus present and of the conditions of temperature in the operation. The absorption maximum occurs at 840 mμ.

The *quantity of reagent* used in the determination has been studied; the optimum amount is found to be 1.5 ml.

The effect of *temperature and time of heating* has been studied; both result in an increase of the sensitivity of the reaction, which reaches a constant value after 15 minutes in a boiling water-bath. Under these conditions Beer's law is applicable in the presence of up to 160 μg of P_2O_5.

A study has been made of the *selectivity* of the method; Ba^{+2}, Pb^{+2}, Sb^{+3} ions, which produce a precipitate under the operating conditions, arsenic, silicon and germanium, which produce analogous reactions, and tungsten, interfere in all proportions. SiO_3^{-2} interferes if present in greater concentration than 100 p.p.m., by producing analogous reaction.

Fe^{+3}, NO_3^-, and $C_2O_4^{-2}$ ions, when present in greater amounts than 20, 20 and 100 p.p.m. respectively, reduce the sensitivity of the reaction.

As a result of these studies, conditions are proposed for the application of the method to routine analysis, for example, the determination of phosphorus in soils[1].

EXPERIMENTAL

Apparatus

Beckman Spectrophotometer D.U., with corex cells of 10 mm path light.
Evans "EEL" Colorimeter.

Reagents

All reagents used are practically free from phosphorus, silicon and germanium and are of analytical reagent grade.

Crystallized ammonium molybdate, sulphuric and hydrochloric acids (Merck *p.a.*) and mercury washed with nitric acid are used.

Solutions

Stock solution of phosphorus (1000 μg P_2O_5 per ml). Dissolve 1.917 g of KH_2PO_4 in 100 ml of water. By suitable dilution a solution containing 10 μg P_2O_5 per ml is obtained.

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Solutions of Mo(VI) and Mo(V). Ammonium molybdate 14.7% (approximately 0.8*M*). A 0.40*M* solution is prepared by suitable dilution. The solution of pentavalent molybdenum is prepared from 50 ml of the 0.80*M* solution of ammonium molybdate to which is added 25 ml of concentrated HCl; the volume is then made up to 100 ml with distilled water and the solution, contained in a volumetric flask, is treated with approximately 10 ml of metallic mercury. The mixture is shaken for five minutes until total reduction to Mo(V) occurs and is then filtered; the solution is of an intense red colour.

General colorimetric process

Except where indicated, all the colorimetric and spectrophotometric determinations are carried out as follows:

The solution of phosphorus contained in a 50 ml volumetric flask is treated with 1.5 ml of reagent, and diluted to approximately 30 ml with distilled water. After warming on the water bath to 98° (except when otherwise indicated) for 15 minutes, the reaction mixture is allowed to cool, then diluted, and the colorimetric measurement is carried out employing a red filter, or the spectrophotometric technique is applied.

In the initial tests, before the appropriate experimental conditions cited were found, experiments were made at 95° for ten minutes. In the colorimetric measurements the extinction is given multiplied by 100.

The influence of the ratio Mo(VI) : Mo(V)

Procedure. Various amounts of reagent are prepared in perfectly dry test tubes, by placing in each of them, 15 ml of *N* sulphuric acid, a constant quantity of pentavalent molybdenum and a variable quantity of molybdate as indicated in Table I.

In all these cases the reaction mixtures assume a yellow coloration before the Mo(VI) is added. On adding the Mo(VI), the tests from No. 7 onwards assume a blue coloration changing to violet; tests Nos. 1 to 6 retain their pale yellow colour.

TABLE I

No.	*Mo(V) 0.40M ml*	*Mo(VI) 0.40M ml*	*Mo(VI) : Mo(V)*
1	0.2	0.1	0.5
2	0.2	0.2	1.0
3	0.2	0.3	1.5
4	0.2	0.4	2.0
5	0.2	0.5	2.5
6	0.2	0.6	3.0
7	0.2	0.7	3.5
8	0.2	0.8	4.0
9	0.2	0.9	4.5
10	0.2	1.0	5.0

Test numbers 1 to 6 so prepared are transferred to 50 ml volumetric flasks, diluted to approximately 30 ml with distilled water and warmed for ten minutes on the water bath. With numbers 1, 2 and 3 the solution does not change colour, with number 4 the solution takes on a weak blue coloration and with numbers 5 and 6 an intense blue. The number 4 test is therefore taken as the limit, indicating for the ratio of Mo(VI) : Mo(V) a value equal to or greater than 2. The blank test is positive in a 0.3*N* sulphuric acid medium under the given conditions.

The behaviour of the different reaction mixtures with phosphorus

The previous tests so obtained (1, 2 and 3) give a blue coloration with solutions of phosphorus, and an increase in the ratio of Mo(VI) : Mo(V) increases the sensitivity of the reaction.

Study of the quantity of acid used for the preparation and stability of the reagent

Tests have been made using several reagents in which the amount of sulphuric and hydrochloric acids varies.

From these tests a mixture was selected of the following composition: Mo(VI) 0.12*M*, Mo(V) 0.08*M*, H_2SO_4 10*N*, and HCl 3*N*; this was studied in detail. Its preparation is as follows:

Preparation of reagent

Weigh 8.15 g of crystallized ammonium molybdate and dissolve in 60 ml of distilled water. Take 25 ml of this solution, add 12.5 ml of 12*N* HCl and dilute with distilled water to 50 ml; add 10 ml of mercury, shake vigorously for five minutes and filter. The solution will have a reddish brown colour. To 30 ml of initial solution of molybdate add 50 ml of 12*N* HCl and 56 ml of 36*N* sulphuric acid, and finally 40 ml of the previously reduced solution, with constant agitation. Dilute with distilled water to 200 ml. The reagent is now ready for use. It is stable for at least six months.

Study of the influence of concentration of phosphorus on the development of colour

This is done according to the general technique at 95° and with a time of heating of 10 minutes. Fig. 1 shows the respective absorption spectra. These data show the formation of a single complex with an absorption maximum of 840 mμ.

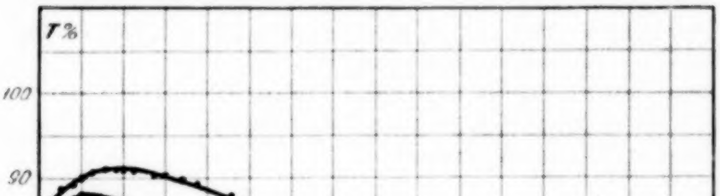

Fig. 1. Absorption spectra of phosphorus.
1) 20 μg of P_2O_5 in 50 ml   3) 70 μg of P_2O_5 in 50 ml
2) 50 ,, ,, ,, ,, ,, ,,   4) 100 ,, ,, ,, ,, ,, ,,
5) 150 μg of P_2O_5 in 50 ml

STUDY OF BEER'S LAW

Influence of the quantity of reagent

The general method is applied, operating at 95° for 10 minutes and changing the quantity of reagent in each experiment. The results of the colorimetric measurements are included in Fig. 2. For more than 1.5 ml the intensity of colour does not change sensibly with increase in the quantity of the reaction mixture.

Therefore, from now onwards the use of 1.5 ml of reaction mixture is adopted, unless otherwise indicated. Under these conditions Beer's law is applicable up to 160 μg of P_2O_5.

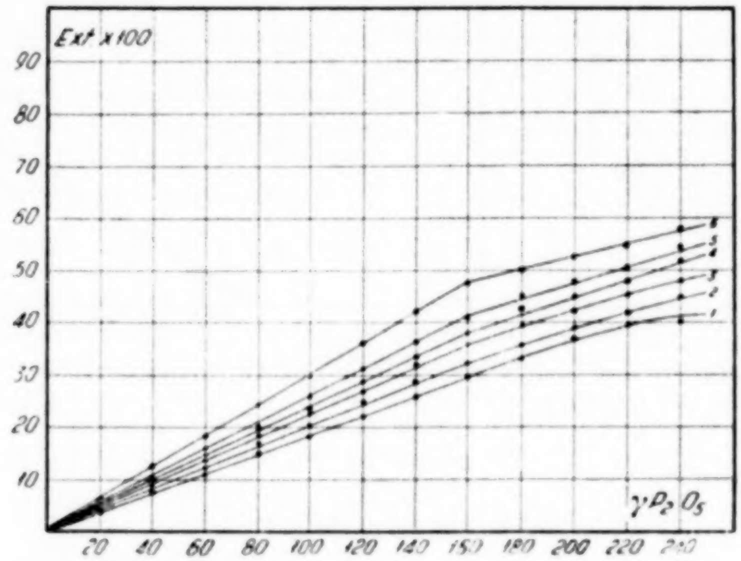

Fig. 2. Effect of the amount of reagent on Beer's law.

1) 0.4 ml of reagent
2) 0.6 ,, ,, ,,
3) 0.8 ,, ,, ,,
4) 1.0 ml of reagent
5) 1.2 ,, ,, ,,
6) 1.5 ,, ,, ,,

Influence of temperature

The general technique is followed and only the temperature is changed.

The results are represented in Fig. 3.

The results obtained show that temperature influences the development of colour considerably although Beer's law is applicable if this is constant. It is essential therefore that the temperature must remain constant. It is proposed to use a boiling water-bath because this makes the procedure more convenient and sensitive.

The slight variations of the temperature of boiling water (because of changes of atmospheric pressure) are not important and are included in experimental errors; they can be compensated easily by standardizing the curve daily whenever variations are suspected.

Influence of time of heating

The validity of Beer's law with regard to time of heating was studied, using the general technique and heating for various periods of time; the results are included in Fig. 4. It is observed that time is an important factor in the development of colour, 15 minutes being necessary for this to reach the maximum.

Study of the interference of some ions

The solution is prepared by the usual technique for colorimetric measurements and variable quantities of the ion whose interference is to be studied are added, to obtain a known concentration in p.p.m. The mixture is finally diluted to 50 ml. In Table II the influence of different ions is summarized.

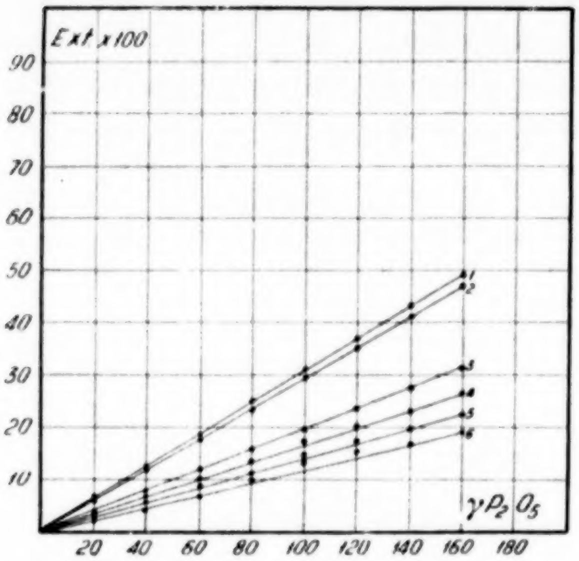

Fig. 3. Effect of temperature on Beer's law.
1) Temperature of 98° (boiling)
2) ,, ,, 95°
3) ,, ,, 85°
4) ,, ,, 75°
5) ,, ,, 65°
6) ,, ,, 55°

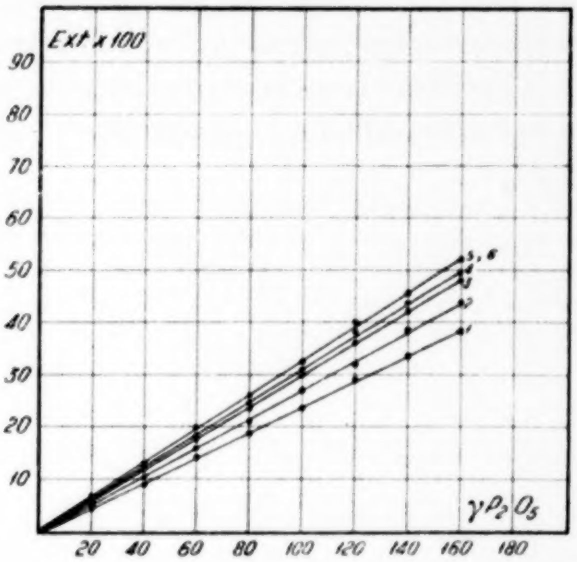

Fig. 4. Influence of time of heating on Beer's law.
1) 5 minutes
2) 8 ,,
3) 10 ,,
4) 12 ,,
5) 15 ,,
6) 20 ,,

TABLE II

Ion	*Added as*	*Maximum amount studied (p.p.m.)*	*Permissible amount (p.p.m.)*	*Effect*
Ca^{+2}	$Ca(CH_3COO)_2$	2000	2000	—
Ba^{+2}	$BaCl_2$	1000	none	precipitated
WO_4^{-2}	Na_2WO_4	1000	,,	blue colour
AsO_4^{-3}	Na_3AsO_4	1000	,,	similar reaction
Pb^{+2}	$Pb(CH_3COO)_2$	550	,,	precipitated
NO_3^-	NH_4NO_3	1000	20	decreases sensitivity
ClO_4^-	$HClO_4$	1000	1000	—
Fe^{+2}	$FeSO_4(NH_4)_2SO_4$	1000	none	decreases sensitivity
Fe^{+3}	$Fe_2(SO_4)_4(NH_4)_2$	1000	,,	,,
$C_2O_4^{-2}$	$Na_2C_2O_4$	1000	100	,,
Sb^{+3}	$SbCl_3$	1000	none	turbidity
Bi^{+3}	$BiCl_3$	100	,,	,,
GeO_3^{-2}	Na_2GeO_3	100	,,	similar reaction
SiO_3^{-2}	Na_2SiO_3	1000	100	,,

DETERMINATION OF ARSENIC AND GERMANIUM

It was expected that it might be possible to determine these elements using a molybdenum reagent similar to that found for phosphorus and with the same advantages. The ratio of Mo(VI) to Mo(V) necessary for the formation of colour was found to be 3 : 2 as in the case of phosphorus.

The characteristics of this reagent in the colorimetric determination of arsenic and germanium have been studied.

In the case of arsenic the absorption spectrum has a maximum absorption at 850 mμ and Beer's law is followed up to 230 μg of As. The absorption spectrum does not change within these limits of concentration. In the case of germanium the absorption maximum is found at 830 mμ and Beer's law holds up to 220 μg of GeO_2. As a result of these studies a similar method to that proposed for phosphorus is proposed for arsenic and germanium.

The reagent has been tested for the determination of silicon, but has not proved suitable, probably because of the high acidity which is necessary.

SUMMARY

A new reagent for the colorimetric and spectrophotometric determination of phosphorus, arsenic and germanium is described. It contains Mo(VI) and Mo(V) in the ratio of 3 : 2 in an acid medium, 10*N* with respect to H_2SO_4 and 3*N* with respect to HCl.

The absorption spectra, the influence of temperature, time, quantity of reagent and selectivity of the method have been studied. Beer's law is applicable up to 160 μg for P_2O_5, 220 μg for GeO_2 and 230 μg for arsenic, in 50 ml.

RÉSUMÉ

Un nouveau réactif est proposé pour le dosage colorimétrique et spectrophotométrique du phosphore, de l'arsenic et du germanium. Il est constitué de molybdène(VI) et de molybdène(V), dans le rapport 3 : 2, en solution acide 10*N* en acide sulfurique et 3*N* en acide chlorhydrique. Une étude a été effectuée sur les spectres d'absorption, l'influence de la température, du temps, de la quantité de réactif et de la sélectivité de la méthode. La loi de Beer est applicable jusqu'à 160 μg pour P_2O_5, 220 μg pour GeO_2 et 230 μg pour As, dans un volume de 50 ml.

ZUSAMMENFASSUNG

Ein neues Reagenz zur kolorimetrischen und spektrophotometrischen Bestimmung von Phosphor, Arsen und Germanium wird beschrieben. Es enthält Mo(VI) und Mo(V) im Verhältnis 3 : 2 in saurer Lösung (10*N* in Schwefelsäure und 3*N* in Salzsäure).

Die Absorptionsspektra, der Einfluss von Temperatur, Zeit und Reagenzmenge und die Selektivität der Methode wurden untersucht. Das Beer'sche Gesetz ist für P_2O_5 bis zu 160 μg, für GeO_2 bis zu 220 μg und für Arsen bis zu 230 μg in 50 ml anwendbar.

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GOLD AND PALLADIUM: THEIR DIETHYLDITHIOCARBAMATE COMPLEXES. COMPOSITION, STRUCTURE AND ANALYSIS

by

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INTRODUCTION

A study of different carbamate complexes obtained with gold and palladium and their behaviour at different pH values is presented here. The compounds obtained with both metals had different compositions and their behaviour towards changes in pH differed. Whilst the behaviour of gold with CBM (= sodium diethyldithiocarbamate) was very dependent on the pH of the solution, that of palladium with CBM was insensitive to changes in pH. This paper presents an extension of our knowledge of auric gold carbamate compounds obtained at different pH values.

The heterometric curves obtained permitted the development of a method for the simultaneous determination of gold and palladium in a single titration, using two critical points obtained from one curve. These results will be presented in the last section of this report.

EXPERIMENTAL

The same method and working conditions were employed as in previous investigations[1]. A summary of the fundamentals of heterometry has been presented[2].

The reagents used were all either AnalaR or chemically pure. The sodium diethyldithiocarbamate (= CBM) was a Fisher Scientific Company certified reagent. Diluted CBM solutions were prepared from an 0.0066*M* stock solution which was stored in a dark brown bottle. The titre of the solution was controlled by titration with a standardized $CuSO_4$ solution at regular intervals.

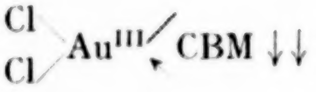
The gold chloride used was a Fisher Scientific Co. solution of $HAuCl_4 \cdot 3H_2O$ (about 51% Au). A stock solution was prepared by mixing 1 ml of the above solution with 50 ml *M* HCl, and was then diluted to 500 ml.

The palladium chloride was a "Palladium Chloride, Fisher S.C. Dry Purified Product". An 0.004*M* stock solution of palladium chloride was prepared. This solution was 0.04*M* in HCl.

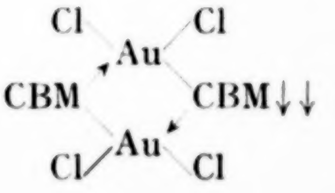
The chloroplatinic acid was a "$H_2[PtCl_6] \cdot x\ H_2O$ Johnson Matthey" reagent. An 0.004*M* stock solution in water was prepared.

Reactions of CBM with auric gold

Auric gold was determined heterometrically both in hydrochloric acid and in nitric acid solution. The first maximum point was always obtained exactly at the molar ratio of 1 Au(III) : 1 CBM. A yellow precipitate was formed which may be presented schematically as $Au_1(CBM)_1$ and whose structure is probably one of the following



(1) or



(2)

($\downarrow\downarrow$ = final maximum optical density point).

Whether or not the titrated solution contained large amounts of neutral salts such as NH_4Cl or NH_4NO_3 made no difference to the results (compare Table I, exps. 1-8 and Fig. 1). Such titrations took about 20 minutes at 20°C. When the titration was carried out in acetic acid solution (Table II and Fig. 2) by the dropwise addition of CBM, the first maximum optical density point coincided with the calculated end-point of the formation of $Au_1^{III}(CBM)_1$ [$Au_m(CBM)_n$ always means molar ratios of gold to CBM in the compound]. On further addition of CBM, the density line then either dropped slightly or remained horizontal until the approximate ratio 1 Au^{III} : 1.5 CBM had been reached, at which point the density dropped abruptly.

The behaviour of auric gold when titrated with CBM in nearly neutral or alkaline solution, was different. Thus, when the gold solution was buffered with Na_2HPO_4 or CH_3COONa, a yellow coloured solution was obtained and no precipitation whatever occurred (Table I, exps. 10-12).

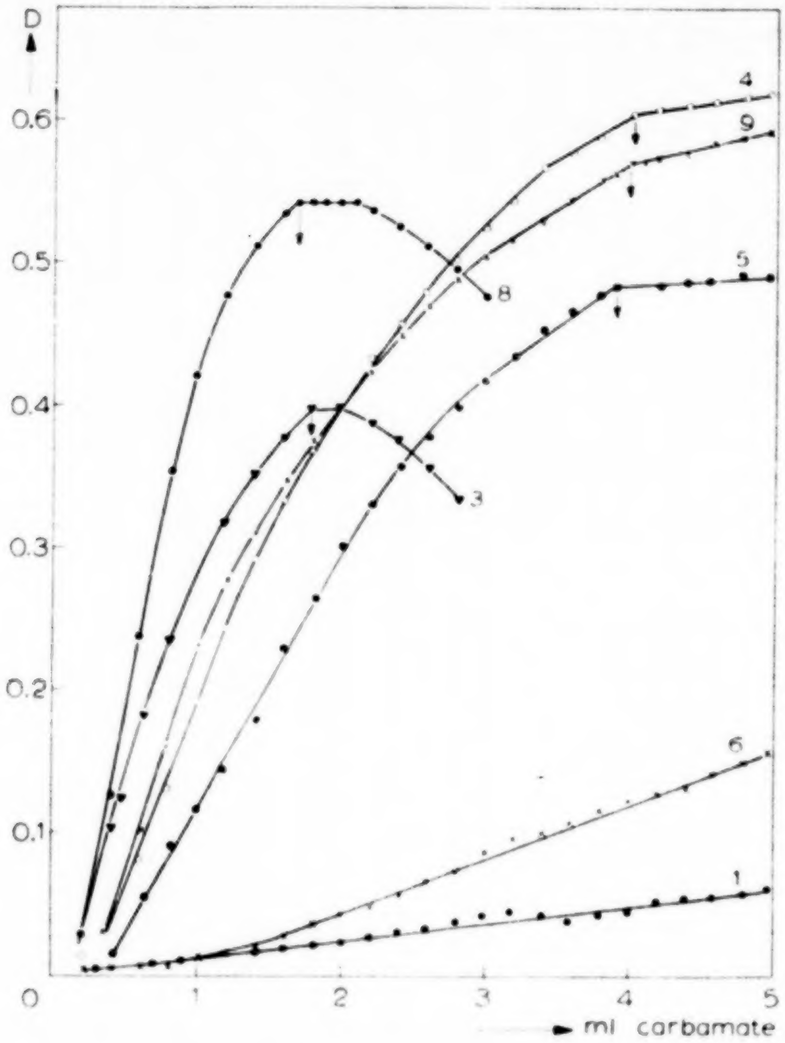


Fig. 1. Titrations of gold with carbamate in mineral acid solutions.

The study of the different gold compounds obtained was of interest to us, both from a general chemical and an analytical standpoint. For this purpose we exploited our experience with other insoluble metal carbamates. The latter were used as indicators of the end-point in those cases where the gold compound studied was either soluble or gave no clear-cut end-point. Of the indicating metals, palladium(II) was very convenient because the $Pd(CBM)_2$ was insoluble both in alkaline and in strong acid solution. It was very interesting to find that each of the different gold carbamate complex compounds was formed quantitatively in a restricted pH-region only and consequently was a very stable complex.

Reactions in acetic acid solution

Table II gives the composition of many titrations carried out with CBM in the presence of gold and palladium together. The curves of some of these titrations are presented in Fig. 2. In each case, when a complete titration was carried out, three critical points were obtained (*A*, *B* and *C*). In all cases, the first maximum point *A* coincided with the point of quantitative formation of $Au_1(CBM)_1$. Somewhat later, approximately when an additional half mole of CBM had been added, a sudden drop in optical density occurred (= point *B*). The location of point *B* on the abscissa varied in each titration and mostly appeared *before* the calculated additional half

TABLE I Composition: *a* ml *mM* $H[AuCl_4]$ + *b* ml 0.002*M* $PdCl_2$ + *c* ml supplements + (20-*a*-*b*-*c*) ml H_2O + *x* ml *nM* CBM. Temp. = 20°C

Exp. no.	Supplements	Molarity of $HAuCl_4$ *m*	$HAuCl_4$ (*a*) ml	$PdCl_2$ (*b*) ml	Au mg	Pd mg	Molarity of CBM	Calculated as CBM		Found			
										CBM at			
								Au ml	Pd ml	initial precip. ml	maxim. point ml	Max. density value	Titration time in min
1	1 ml *M* HCl + 1 ml 2*M* NH_4Cl	0.0011	5	6	1.1	1.28	0.00135	4.0				0.05	17
2	1 ,, ,, ,, + 1 ,, 2*M* ,,	0.0011	5	1	1.1	0.21	0.004	1.7		0.2	1.65	0.60	13
3	1 ,, ,, HNO_3 + 1 ,, 2*M* NH_4NO_3	0.0011	5	1	1.1	0.21	0.004	1.7		0.2	1.75	0.39	22
4	1 ,, ,, HCl + 5 ,, 2*M* NH_4Cl	0.0016	5	2	1.57	0.42	0.002	4.0		0.4	4.00	0.60	24
5	1 ,, ,, ,, ,, + 1 ,, 2*M* ,,	0.0016	5	2	1.57	0.42	0.002	4.0			3.90	0.48	25
6	1 ,, ,, ,, + 1 ,, 2*M* ,,	0.0016	5	8	1.57	1.7	0.002					0.15	28
7	1 ,, ,, ,,	0.0016	5	1	1.57	1.7	0.002	4.0		0.4	3.8	0.50	30
8	1 ,, ,, HNO_3	0.0011	5	1	1.1	0.21	0.004	1.7		0.2	1.7	0.54	10
9	1 ,, ,, HCl + 2 ml 2*M* NH_4Cl + 4 ml 0.004*M* $H_2[PtCl_6]$	0.0016	5		1.57		0.002	4.0		0.2	4.00	0.59	27
10	2.5 ,, 4*M* NH_4Cl + 8 ml 0.2*M* Na_2HPO_4	0.0011	5	3	1.1	0.64	0.005	2.7	2.4	2.6	5.2	0.51	55
11	2.5 ,, 4*M* ,, + 8 ,, 0.2*M* ,,	0.0016	4	5	1.26	1.06	0.0066	2.3	3.0	2.2	5.3	0.70	40
12	2.5 ,, 4*M* ,, + 8 ,, 0.2*M* ,,	0.0011	3	5	0.65	1.06	0.0066	1.15	3.0	1.1	4.1	0.75	38

TABLE II Composition: *a* ml 0.002*M* $PdCl_2$ + 4 ml 0.0016*M* $HAuCl_4$ + 1.5 ml 0.2*M* CH_3COONa + *b* ml *M* CH_3COOH + 5 ml *mM* NH_4Cl + *c* ml supplements + (9.5-*a*-*b*-*c*) H_2O + *x* ml *nM* CBM. Temp. = 20°C

Exp. no.	Supplements	$PdCl_2$ ml	CH_3COOH ml	Molarity of CBM	Molarity of NH_4Cl	Found							Titration time in min
						At first maximum point			Density drop at ml	At second maximum point			
							ml CBM				ml CBM		
						density	calc.	found		Density	calc.	found	
13	— —	5	4	0.0066	4	0.46	1.36	1.35	1.9	0.30	4.93	4.90	16
14	5 ml 0.004*M* H_2PtCl_6	5	4	0.0066	4	0.14	1.36	1.35	no	0.60	4.93	>6.5	25
15	2 ,, 0.004 ,, ,,	5	4	0.0066	4	0.34	1.36	1.36	1.8	0.42	4.90	5.8	18
16	— —	5	2	0.0066	2	0.30	1.36	1.40	1.6	0.30	4.93	4.8	18
17	— —	5	2	0.0066	4	0.38	1.36	1.35	1.5	0.34	4.93	4.90	19
18	— —	8	2	0.0066	2			?	2.2			?	
19	— —	3	2	0.0066	2	0.39	1.36	1.30	1.7	0.24	3.75		17
20	— —	5	4	0.0066	2	0.33	1.36	1.35	1.8	0.35	4.93	5.04	17
21	— —	3	4	0.0066	2	0.44	1.36	1.40	1.8	0.26	3.75	3.7	17
22	— —	3	4	0.0037	2	0.22	2.40	2.36	3.6	—	—	—	17
23	— —	5	4	0.0037	2	0.25	2.40	2.40	3.6	—	—	—	13

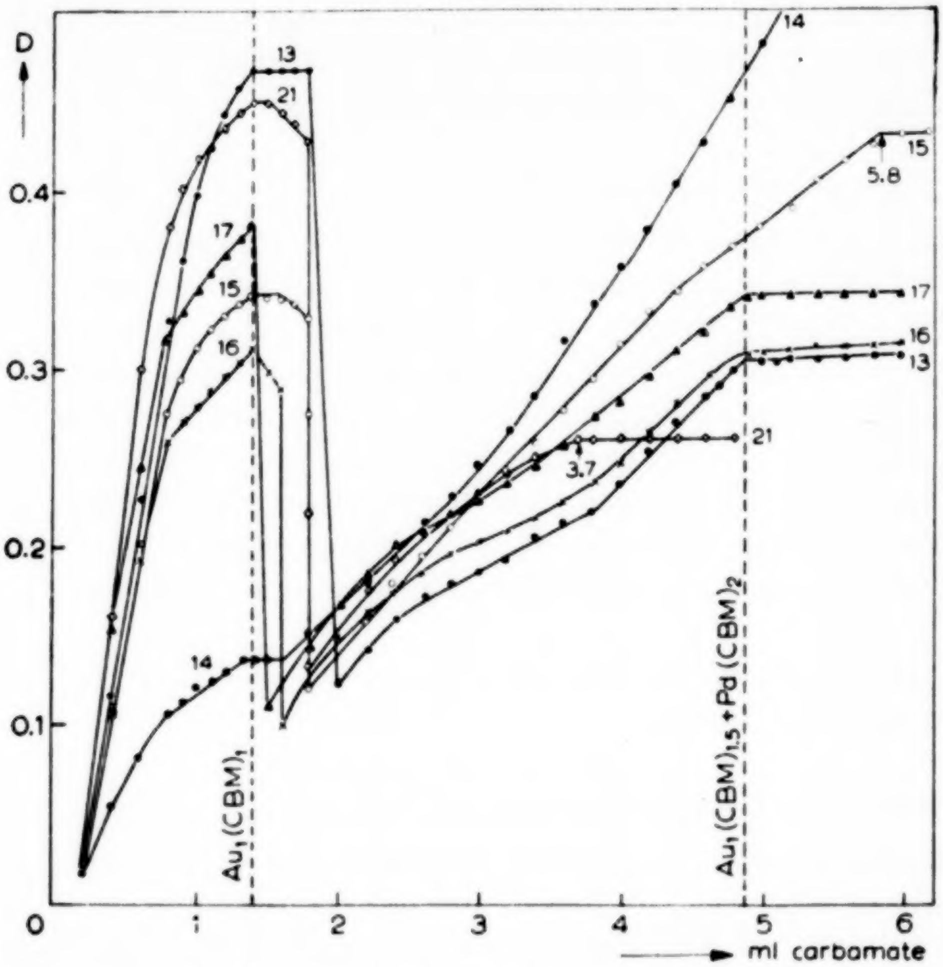


Fig. 2. Titrations of gold and palladium with carbamate in acetic acid solution.

mole of CBM had been added. (When the amount of added palladium was large (exp. 18) this point coincided with the calculated point, $Au_1(CBM)_{1.5}$, but in this case the points *A* and *C* could no longer be located with certainty.) Also, when the titration was carried out with a more dilute CBM solution (exps. 22, 23) the point *B* exactly coincided with that calculated for the formation of $Au_1(CBM)_{1.5}$. The compound obtained at the calculated second critical point (*B*) evidently has the composition $Au_2(CBM)_3$.

The theoretical location of *B* (obtained by calculation from *A*) was of importance in calculating the amount of palladium present. $Pd(CBM)_2$ precipitates quantitatively immediately after the formation of $Au_1(CBM)_{1.5}$. Thus, after *B*, the density rose because of the precipitation of $Pd(CBM)_2$ quantitatively and completely at *C*. $Pd(CBM)_2$ may be represented as:

$$\left[\mathrm{CBM} \diagdown\!\!\nearrow \mathrm{Pd} \swarrow\!\!\diagdown \mathrm{CBM}\right]^{0} \downarrow\downarrow \quad \ldots\ldots\ldots\ldots\ldots \quad (3)$$

In all cases, after the point *C*, a horizontal maximum density line was obtained and no further reaction with CBM was detected. The last point *C* corresponds exactly to the end of the three reactions which occurred in the heterogeneous system successively and quantitatively.

As Table II shows, a full titration does not take more than 15-20 minutes at 20°C. As to the influence of neutral salts, it was found that the presence of large amounts of chloride was essential in order to carry out the titrations. Besides, the pH of the solution must be as close as possible to the pH of pure CH_3COOH. When $H_2[PtCl_6]$ was present in these solutions (exps. 14 and 15) the point "C" gave the end of the reaction of CBM with both palladium and platinum.

Reactions in strongly acid solution

Table I, exps. 1-8 presents the compositions and the results of such titrations. Comparing the results of experiments 2 and 3 it can be seen that in the presence of nitrate, the maximum density value was depressed. On the other hand, when somewhat less palladium was present in the solution (compare exps. 4 and 5) the maximum density value was higher with the higher concentration of NH_4Cl. The amount of palladium must always be greatly restricted. When it was in high concentration (exps. 1 and 6) the maximum density value was very low and no critical point at all was obtained. The same applied when a neutral electrolyte was absent: the presence of the palladium reduced the densities and made the titration of gold impossible.

As exp. 9 shows, gold can be titrated in the presence of $H_2[PtCl_6]$ giving the first maximum point at $Au_1(CBM)_1$.

Reactions in neutral and alkaline solution

As seen previously, no precipitation of gold occurred from solutions containing sodium acetate or Na_2HPO_4. It was of interest to investigate the reaction to see how far the soluble compound was formed quantitatively and to determine the composition of the soluble gold compound.

To the gold chloride solution containing sodium acetate was added one ml 0.01*M* of the following salts: $CuSO_4$, $CdSO_4$, $ZnSO_4$ and $NiSO_4$. The gold was titrated and the point of the initial precipitation of the indicator metal carbamate was obtained at the intersection of the first part of the density line with the abscissa. This was most successful with $ZnSO_4$ whilst Cd^{+2} and Cu^{+2} gave precipitation nearly at the beginning of the titration. It was ascertained that the point of the initial precipitation lay at the ratio 1 Au^{III} : 2 CBM^-. Therefore it may be concluded that the soluble gold compound obtained had the composition $[Au^{III}\,(CBM)_2]^+$.

The reaction concerned may be represented as follows:

$$[AuCl_4]^- + 2\,(CBM)^- \rightarrow [AuCBM_2]^+ \uparrow + 4\,Cl^- \;.\;.\;.\;.\;. \quad (4)$$

The complex obtained presumably has the structure:

$$\left[\mathrm{CBM}\overset{\diagdown}{\underset{\nearrow}{}}\mathrm{Au^{III}}\overset{\swarrow}{\underset{\diagdown}{}}\mathrm{CBM}\right]^{+} \;.\;.\;.\;.\;.\;.\;.\;.\;.\;.\;.\;.\;.\;.\;.\;. \quad (5)$$

Similar titrations were carried out in which known amounts of palladium chloride were added to the gold solutions containing sodium acetate or Na_2HPO_4. The best results were obtained in the presence of phosphate. Table I (exps. 10-12) shows the composition of these experiments and the results obtained. The course of the reaction may be seen in Fig. 3. These solutions contained comparatively large amounts of palladium. *Two* critical points were obtained (the point of initial precipitation and that of the first maximum density point). The first point gave the amount of gold calculated as $[Au_1CBM_2]^+$ and the second point gave the sum of $[Au(CBM)_2]^+ + Pd(CBM)_2 \downarrow\downarrow$.

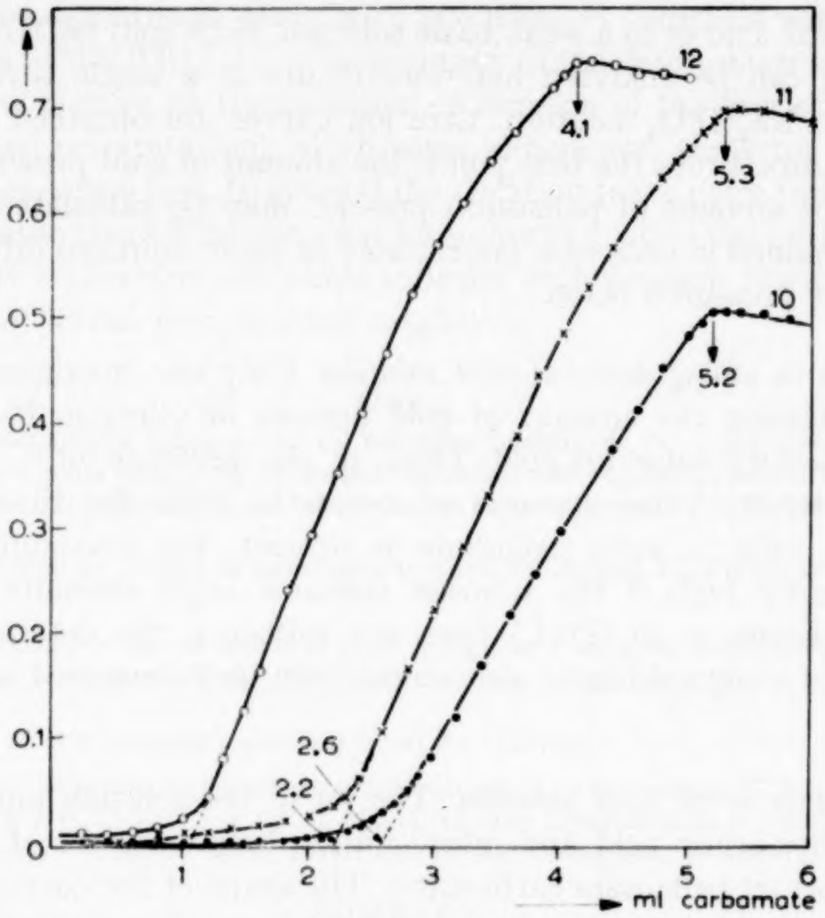


Fig. 3. Titrations of gold and palladium with carbamate in alkaline solution.

The reaction may be presented as follows:

$$a[\mathrm{AuCl_4}]^- + b\,\mathrm{PdCl_2} + 2\,(a+b)\,(\mathrm{CBM})^- \rightarrow a\,[\mathrm{Au(CBM)_2}]^+ + b\,\mathrm{Pd(CBM)_2}\downarrow\downarrow + 2\,(2a+b)\,\mathrm{Cl}^- \quad \ldots\ldots\ldots\ldots \quad (6)$$

Although both reactions occurred without delay, more time was needed for a titration as care had to be taken to fix the point of initial precipitation with certainty.

Solubility in organic reagents

The insoluble compounds $\mathrm{Au_1(CBM)_1}$ and $\mathrm{Pd(CBM)_2}$, obtained heterometrically in mineral acid solution were separated from the solution by centrifugation. The $\mathrm{Au_1(CBM)_1}$ was a bright yellow powder; the $\mathrm{Pd(CBM)_2}$ was a fine flesh-coloured powder. Their solubility in organic reagents was tested giving the following results:

$Au_1(CBM)_1$ is apparently insoluble in $\mathrm{CCl_4}$ and $\mathrm{CS_2}$, slightly soluble in dioxan and ethyl ether, and easily soluble in $\mathrm{CHCl_3}$, acetone, methyl and ethyl alcohol, giving yellowish solutions.

$Pd(CBM)_2$ is apparently insoluble in $\mathrm{CCl_4}$, slightly soluble in methyl and ethyl alcohol, soluble in part in $\mathrm{CS_2}$ and easily soluble in dioxan, $\mathrm{CHCl_3}$ and acetone, giving a yellow solution.

Analytical aspects

The reactions presented above and the calculated results compiled in the tables and figures (the same numeration is used in both cases) show that in strongly mineral acid solution, only gold can be determined in a mixture containing palladium and platinum. In acetic acid or in a weak basic solution, both gold (as $HAuCl_4$) and palladium (as $PdCl_2$) can be analysed heterometrically in a single titration. Either in acetic acid or in Na_2HPO_4 solution, titration curves are obtained which give two sharp critical points. From the first point, the amount of gold present, and from the second point, the amount of palladium present, may be calculated. The character of the curves obtained in each case (acetic acid or basic solution) differ. Their merits and demerits are presented below.

Determination in strong mineral acid solution. Only one maximum density point is obtained indicating the amount of gold present in solution. Palladium reduces the maximum density value for gold. Thus, in the presence of $\sim$ 50% palladium, the maximum density value becomes so low as to make the titration impossible. However, when only $\sim$ 20% palladium is present, the maximum density value remains sufficiently high if the solution contains large amounts of NH_4Cl. The presence of platinum as $H_2[PtCl_6]$ does not influence the determination of gold (see Table I). 1-1.5 mg gold in 20 ml solution can be determined with an error between 0-2%.

Determination in acetic acid solution. The pH of the solution must be very close to the pH of pure acetic acid and must contain large excesses of neutral chloride (see special report on palladium carbamate). The shape of the curve obtained is very convenient (in contrast to the shape obtained in weakly basic solution) because it posesses two maximum density points each corresponding respectively to the exact amount of gold and palladium in solution. It must be considered that generally in heterometry it is much easier to locate a critical point as a "first maximum density point" than as a "point of initial precipitation". Although the maximum density values at both critical points sometimes do not differ greatly, both points can be determined with precision. This is due to the density drop which occurs after the first critical point (and is caused by the transformation of $Au_1(CBM)_1 \downarrow\downarrow$ into $Au_1(CBM)_{1.5} \uparrow$ or $Au_2(CBM)_3 \uparrow$. Both metals can be determined with the same precision and the error is generally between 0-2%. A full titration takes 15-20 minutes. The first critical point indicates the quantitative formation of $Au_1(CBM)_1 \downarrow\downarrow$ whilst the second point corresponds to the quantitative formation of $Pd(CBM)_2 \downarrow\downarrow$.* It is interesting to note that when the solution contains some platinum as $H_2[PtCl_6]$ in addition, the second critical point is obtained when both metals (palladium and platinum) are quantitatively formed. (This case will be discussed in a special report on platinum carbamate.)

Determination in weakly basic solution. The solution must be buffered either with an excess of sodium acetate or with an excess of Na_2HPO_4. In the latter case, the results are more reliable. The first critical point is obtained at the intersection of the abscissa with the line drawn through the first part of the palladium carbamate density line; it corresponds to the quantitative formation of $[Au(CBM)_2]^+$ in solution. The second critical point coincides with the first maximum density point, after which a horizontal maximum density line is obtained. This point is highly reproducibl and can always be determined easily with precision. It coincides with the quantitative formation of $[Pd(CBM)_2]^\circ\downarrow\downarrow$. The accuracy of the determination of both metals depends therefore entirely on the accuracy of location of the first critical point (*i.e.* the point of initial precipitation). With some experience, the error of the location of the first point becomes low. In general the titration takes more time than in acetic acid solution because there is no criterion for indicating when the initial precipitation will commence. It is therefore advisable to begin with a rough titration in order to locate the point of initial precipitation roughly.

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* This second point therefore corresponds to the sum of $Au_1(CBM)_{1.5}$ + $Pd(CBM)_2$.

Method

1. *In strong mineral acid solution.* 20 ml solution containing $\sim$ 1 mg gold as $H[AuCl_4]$, in addition to $PdCl_2$ (not more than 20% of the gold content) and $H_2[PtCl_6]$ (which may be in excess), $\geqslant$ 1 ml *M* HCl and $\sim$ 0.5 g NH_4Cl are titrated with 0.001-0.0015*M* CBM. The titration time is about 20 minutes.

Remark: The addition of NH_4Cl is unnecessary when $PdCl_2$ and $H_2[PtCl_6]$ are present in small quantities.

2. *In acetic acid solution.* 20 ml solution containing: $\sim$ 1 mg gold as $H[AuCl_4]$, $\sim$ 1 mg palladium as $PdCl_2$, about 1 ml glacial CH_3COOH and 0.5-1.0 g NH_4Cl are titrated with 0.002-0.006*M* CBM.

Remark: The pH of the analysed solution must be $\sim$ 3.0.

3. *In weakly basic solution.* 20 ml solution containing: $\sim$ 1 mg gold as $H[AuCl_4]$ $\sim$ 1 mg palladium as $PdCl_2$, 0.5 g NH_4Cl and 1-2 ml *M* Na_2HPO_4 are titrated with 0.002-0.006*M* CBM.

Remark: The solution must be neutralized before the phosphate is added.

SUMMARY

A study was made of the composition and behaviour of complexes formed at different pH's between gold(III) and palladium(II) with sodium diethyldithiocarbamate. The complexes obtained are: $Pd(CBM)_2$ (insoluble); $[Au(CBM)]^{+2}$ (insoluble); $[Au_2(CBM)_3]^{+3}$ (soluble); $[Au(CBM)_2]^+$ (soluble).

Analytical methods are presented for the determination of gold and palladium in mixtures. The heterometric curves obtained permit the determination of gold as well as of palladium in a single titration, with an error of 0-2%.

RÉSUMÉ

Une étude a été effectuée sur la constitution et le comportement des complexes formés entre l'or(III), le palladium(II) et le diéthyldithiocarbamate de sodium à différents pH. Les composés obtenus sont: $Pd(CBM)_2$ (insoluble); $[Au(CBM)]^{+2}$ (insoluble); $[Au_2(CBM)_3]^{+3}$ (soluble), $[Au(CBM)_2]^+$ (soluble).

Des méthodes sont décrites pour le dosage de l'or et du palladium. Les courbes hétérométriques obtenues permettent le dosage de l'or et du palladium, l'un en présence de l'autre, par un seul titrage, avec une erreur de 0-2%.

ZUSAMMENFASSUNG

Die Zusammensetzung und das Verhalten der Gold(III)- und Palladium(II)-Komplexe mit Natriumdiäthyldithiocarbamat, die bei verschiedenen pH-Werten erhalten werden, wurde studiert. Die erhaltenen Komplexe waren: $Pd(CBM)_2$ (unlöslich); $[Au(CBM)]^{+2}$ (unlöslich); $[Au_2(CBM)_3]^{+3}$ (löslich); $[Au(CBM)_2]^+$ (löslich).

Analytische Methoden für die Bestimmung von Gold und Palladium in Gemischen wurden beschrieben. Die erhaltenen heterometrischen Kurven erlauben die Bestimmung, sowohl von Gold als auch von Palladium, in einer einzigen Titration, mit einem Fehler von 0-2%.

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MICRO-HETEROMETRIC DETERMINATION OF BISMUTH WITH SODIUM DIETHYLDITHIOCARBAMATE

by

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INTRODUCTION

In this paper a method is presented for the determination of bismuth. In the presence of many metals, difficulties were encountered and generally the density increased continuously after the calculated end-point had been reached. By the use of a mixture of appropriate complexing agents in suitable amounts, good results were achieved except in the case of copper and antimony. A small selection of experiments made is presented, but in order to save space there is no discussion of the way in which we arrived at reaction conditions for each experiment as specified in the table. In order to hold the bismuth in solution, excess of ammoniacal citrate or tartrate was added at the beginning of titration. Because of this, the amount of foreign metal which could be present without using up the citrate was governed by the amount of the latter in solution.

EXPERIMENTAL

The same working conditions were observed as in previous heterometric investigations[1]. The fundamentals of heterometry are presented elsewhere[2]. All titrations were carried out at 20°C; the volume was 20 ml and the diameter of the cylindrical reaction vessel was about 4 cm. The velocity of stirring, which was the maximum consistent with stable measurements of the galvanometer, was controlled electronically, being more or less uniform in all experiments.

All reagents used were either analytical or chemically pure reagents. The bismuth nitrate was a Baker's c.p. analysed reagent, $Bi(NO_3)_3 \cdot 5H_2O$. A stock solution of sodium diethyldithiocarbamate (= CBM) (Fisher pure reagent) was prepared by weighing out a calculated amount of the salt and dissolving it in water. More dilute solutions were prepared every few days. They were standardised with a copper sulphate solution of known titre.

In almost all cases the analytical end-point of the titration was fixed, from enlarged titration density curves, directly by the intersection of a line drawn through the points of the last part (∿ last quarter of the titration curve) with the horizontal maximum density line. Only in a few cases was the contact point of both lines taken instead as the end-point.

Method

20 ml of the analysed solution containing ∿ 2 mg bismuth in addition to other supplements, is titrated with ∿ 0.0066*M* CBM. The end-point is obtained from enlarged titration curves by the intersection of the line of the last part of the titration curve with the maximum density line. Titration time 10-15 minutes. The error is generally small.

The analysed solution contains the following supplements:

1. ⩾ 5 *ml M* Ma_3*-citrate* + 1 *ml conc. ammonia* (in the absence of foreign metals or in the presence of Ca^{+2}, Ba^{+2}, Mg^{+2} or Fe^{+3}).
2. 5 *ml M* K_2*-tartrate* + 1 *ml conc. ammonia* (in the presence of Cr^{+3}).

3. *1 ml M K_2-tartrate + 1 ml conc. ammonia + a ml 3M KCN* (in the presence of Zn^{+2}, Ni^{+2}, Cd^{+2}, Hg^{+2}, Ag^{+}).
4. *12 ml 0.2M Na_2H_2-EDTA + 1 ml conc. ammonia* (in the presence of Mn^{+2}, Co^{+2}, Al^{+3}, Pb^{+2}).

RESULTS AND DISCUSSION

The following complexing agents were used in strongly ammoniacal solution: trisodium citrate, dipotassium tartrate, Na_2H_2-ethylediamine tetraacetate (Na_2H_2-EDTA) and potassium cyanide.

Composition: Without exception, in all titrations of bismuth with carbamate, the end-point of the titration was found at the molar ratio of 1 Bi : 2 CBM without dependence on the complexing agent used. In all cases a bright yellow flocculant precipitate was obtained. It can therefore be assumed that the complexing agent does not participate in the formation of the insoluble compound, which is insoluble in ∼ 25% alcohol (exp. 6) but dissolves in ∼ 25% dioxan (exp. 5). A parallel pH-heterometric study showed that the above compound is insoluble at all pH values.

Analytical study: In Table I and Fig. 1 are compiled the results of experiments carried out in order to investigate the conditions necessary for the quantitative determination of bismuth. Also taking into consideration the results of experiments

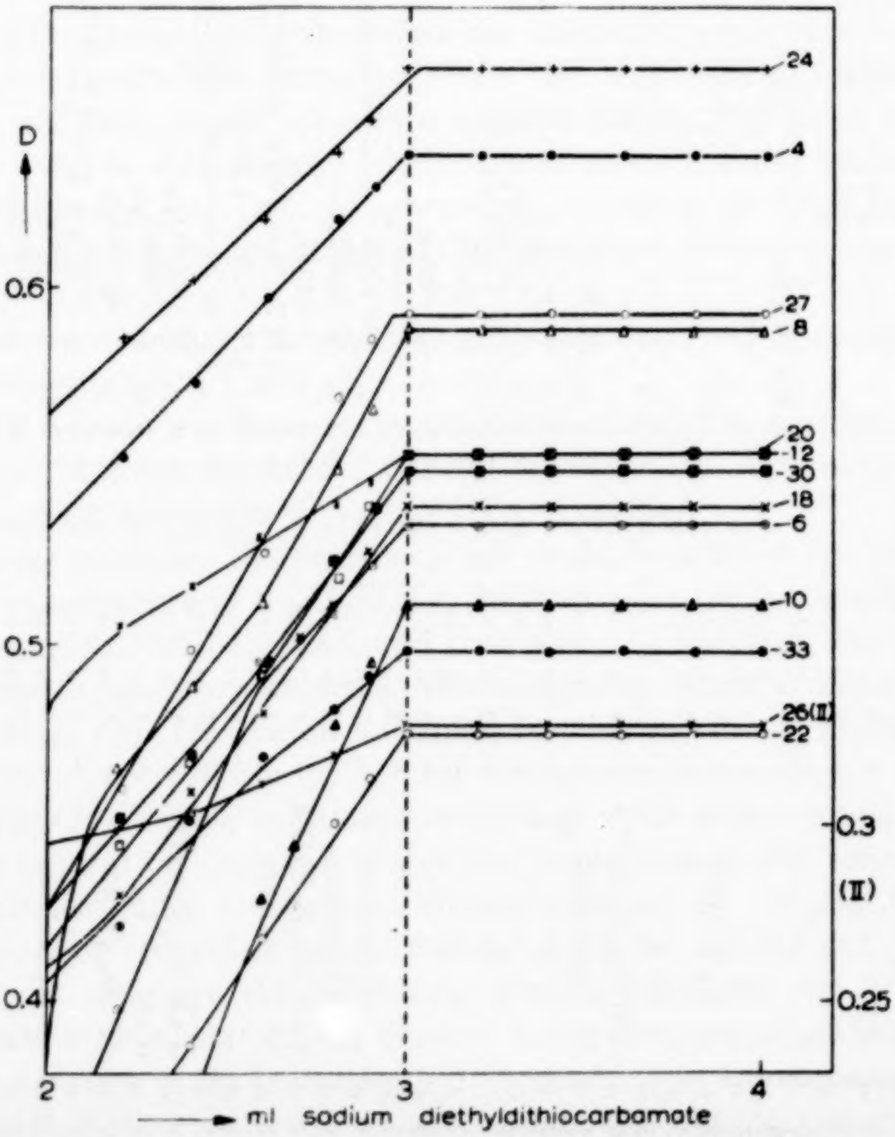

Fig. 1. Titration curves of bismuth nitrate with sodium diethyldithiocarbamate.

TABLE I Composition: 5 ml 0.002M Bi(NO$_3$)$_3$ + (15-a) ml supplements + a ml H$_2$O + x ml 0.0066M sodium diethyldithiocarbamate (= CBM). Content: 2.09 mg Bi. Temp. = 20°C

Exp. no.	*Supplements*	*Bi %*	*ml CBM found (x)*	*Initial precip. at ml*	*Maxim. density value*	*Approx. titration time in min*	*% error*
1	1 ml M Na$_3$-citrate + 0.5 ml NH$_3$ conc.			0.2	0.42	17	fl *
2	1 ,, ,, ,, + 1 ,, ,, ,,		3.00	0.2	0.50	12	0.0
3	5 ,, ,, ,, + 1 ,, ,, ,,		2.97	0.2	0.64	16	1.0
4	5 ,, ,, ,, + 2 ,, ,, ,,		3.00	0.2	0.63	16	0.0
5	5 ,, ,, ,, + 1 ,, ,, ,, + 5 ml dioxan			∞	0.0	10	
6	1 ,, ,, ,, + 1 ,, ,, ,, + 5 ,, alc.		3.00	0.4	0.53	11	0.0
7	1 ,, ,, K$_2$-tartrate + 1 ,, ,, ,,		2.90	0.2	0.54	12	3.3
8	5 ,, ,, ,, + 1 ,, ,, ,,		2.97	0.4	0.57	9	1.0
9	5 ,, ,, ,, + 1 ,, ,, ,, + 5 ,, ,,		2.96	0.4	0.60	13	1.0
10	10 ,, 0.2M Na$_2$H$_2$-EDTA + 1 ,, ,, ,,		3.00	1.2	0.51	25	0.0
11	1 ,, M Na$_3$-citrate + 1 ,, ,, ,, + 5 ,, M KCN		2.90	0.4	0.50	10	—3.3
12	3 ,, ,, ,, + 1 ,, ,, ,, + 5 ,, ,, ,,		3.00	0.4	0.55	13	0.0
13	5 ,, ,, ,, + 1 ,, ,, ,, + 3 ,, ,, Ca(NO$_3$)$_2$	1.7	3.00	0.2	0.41	16	0.0
14	1 ,, ,, ,, + 0.5 ,, ,, ,, + 5 ,, 2M Ca(NO$_3$)$_2$	0.6	2.92	0.4	0.43	12	2.7
15	9 ,, ,, ,, + 1 ,, ,, ,, + 3 ,, M BaCl$_2$	0.5	2.96	0.6	0.50	11	1.0
16	5 ,, ,, ,, + 1 ,, ,, ,, + 3 ,, ,, MgCl$_2$	3.4	3.00	0.2	0.50	13	0.0
17	9 ,, ,, ,, + 1 ,, ,, ,, + 5 ,, ,, ZnSO$_4$	0.6	∞	0.2	0.56	11	
18	1 ,, ,, K$_2$-tartrate + 1 ,, ,, ,, + 10 ,, 3M KCN + 2 ml 2M ZnSO$_4$	0.8	3.00	0.2	0.53	15	0.0
19	7 ,, ,, Na$_3$-citrate + 1 ,, ,, ,, + 2 ,, M MnCl$_2$	1.9					fl *
20	12 ,, 0.2M Na$_2$H$_2$EDTA + 1 ,, ,, ,, + 2 ,, ,, MnCl$_2$		3.00	0.8	0.55	12	0.0
21	1 ,, M K$_2$-tartrate + 1 ,, ,, ,, + 7 ,, 3M KCN + 2 ml M Ni(NO$_3$)$_2$	1.7	3.00	0.4	0.62	6	0.0
22	1 ,, ,, ,, + 1 ,, ,, ,, + 10 ,, 3M KCN + 4 ml M ,,	0.8	3.00	0.4	0.48	12	0.0
23	1 ,, ,, ,, + 1 ,, ,, ,, + 7 ,, 3M KCN + 2 ml M Co(NO$_3$)$_2$		∞		0.0		
24	12 ,, 0.2M Na$_2$H$_2$EDTA + 1 ,, ,, ,, + 2 ,, M Co(NO$_3$)$_2$	1.7	3.00	0.2	0.66	11	0.0
25	12 ,, 0.2M ,, + 1 ,, ,, ,, + 2 ,, ,, Fe(NO$_3$)$_3$	1.8	2.90	1.2	0.36	10	—3.3
26	7 ,, M Na$_3$-citrate + 1 ,, ,, ,, + 3 ,, ,, Fe(NO$_3$)$_3$	1.3	3.00	0.4	0.33	14	0.0
27	7 ,, ,, ,, + 1 ,, ,, ,, + 2 ,, ,, MgCl$_2$ + 3 ml M Fe(NO$_3$)$_3$		2.95	0.2	0.62	18	1.6
28	5 ,, ,, K$_2$-tartrate + 1 ,, ,, ,, + 0.5 ,, ,, Cr(NO$_3$)$_3$	7.5	3.00	0.4	0.32	13	0.0
29	7 ,, ,, ,, + 1 ,, ,, ,, + 2 ,, ,, Al(NO$_3$)$_3$	3.7					fl *
30	12 ,, 0.2M Na$_2$H$_2$EDTA + 1 ,, ,, ,, + 2 ,, ,, ,,		2.99	1.0	0.55	11	0.3
31	1 ,, M K$_2$-tartrate + 1 ,, ,, ,, + 9 ,, 3M KCN + 4 ml M Cd(NO$_3$)$_2$	0.5	3.00	0.4	0.59	12	0.0
32	7 ,, ,, Na$_3$-citrate + 1 ,, ,, ,, + 2 ,, M Pb(NO$_3$)$_2$		∞	0.2	>0.52	5	
33	12 ,, 0.2M Na$_2$H$_2$EDTA + 1 ,, ,, ,, + 2 ,, ,, Pb(NO$_3$)$_2$	0.5	3.00	1.8	0.50	10	0.0
34	1 ,, M K$_2$-tartrate + 1 ,, ,, ,, + 6 ,, 3M KCN + 7 ml 0.2M Hg(NO$_3$)$_2$	0.7	3.00	0.2	0.55	6	0.0
35	1 ,, ,, ,, + 1 ,, ,, ,, + 3 ,, 3M KCN + 2 ml 0.5M AgNO$_3$	1.9	3.00	0.6	0.59	10	0.0

* fl = fluctuation

not cited in the Table, the following conclusions may be drawn: bismuth can be successfully determined heterometrically in the presence of the following cations: Ca^{+2}, Ba^{+2}, Mg^{+2}, Zn^{+2}, Mn^{+2}, Ni^{+2}, Co^{+2}, Fe^{+3}, Cr^{+3}, Al^{+3}, Cd^{+2}, Pb^{+2}, Hg^{+2} and Ag^{+}.

In the absence of foreign metals the determination can be made successfully in the presence of a large excess of *citrate* or *tartrate* in addition to ammonia (exps. 4 and 8). In the presence of 25% of alcohol the titration was smooth (exps. 6 and 9), but in 25% of dioxan the bismuth compound is entirely soluble (exp. 5). In the presence of ammoniacal Na_2H_2EDTA the error was small but the initial precipitation occurred very late, *i.e.* only after the addition of 2/3 of the amount of titrant theoretically required for complete precipitation. The titration time was longer (exp. 10). Large amounts of *potassium cyanide* had no influence on the titration (exps. 11 and 12).

The presence of foreign metals generally had no influence on the maximum density value obtained, as was also the case when the foreign salts were present as chloride, nitrate or sulfate. *Calcium nitrate* and *barium chloride* both made up more than 99% of the total metal content and had no noticeable influence, (exps. 13-15). Moderate amounts (∼ 96%) of *magnesium chloride* were without influence (exp. 16) but when the amount of magnesium was much greater, the end-point was no longer sufficiently precise because the density values fluctuated. In ammoniacal citrate solutions with *zinc sulfate*, whatever the excess of citrate present, the end-point was uncertain and the density increased after the calculated end-point had been reached (exp. 17). Good results were obtained when the ammoniacal tartrate (or citrate) contained, in addition, excess potassium cyanide (Zn: 99.2%) (exp. 18). In excesses of *manganese chloride* with citrate, whether potassium cyanide was present or not, the results fluctuated (exp. 19). In ammoniacal solution of Na_2H_2EDTA a smooth titration with a small error was obtained. The initial precipitation occurred somewhat late (exp. 20).

Good results were obtained in solutions of *nickel nitrate* which contained potassium cyanide in excess (exps. 21 and 22).

When *cobalt nitrate* was present in solutions containing potassium cyanide, no precipitation of bismuth occurred (exp. 23). Good results were obtained in a cobalt solution containing ammoniacal Na_2H_2EDTA (exp. 24).

In *iron nitrate* solutions the determination could be carried out either in ammoniacal citrate or ammoniacal Na_2H_2EDTA. In both cases the maximum density value was low (exps. 25 and 26). It was found that when, in addition, the citrate solution contained some magnesium chloride, the maximum density value obtained was much higher (exp. 27). The reason for this is to be found in the presence of chloride anions.

In chromium(III) nitrate solutions containing 1 ml molar solution or more of chromium, precipitation occurred before the beginning of the titration when the solutions contained large amounts of citrate, tartrate or Na_2H_2EDTA. With a reduced amount of chromium, the titration could be carried out in ammoniacal tartrate solution, although the maximum density value was low (exp. 28).

In *aluminium nitrate* solution the density values fluctuated in citrate or tartrate solution. The titration could be carried out successfully in ammoniacal Na_2H_2EDTA. The initial precipitation occurred somewhat late but the maximum density value was normal (exp. 30).

References p. 492

In *cadmium nitrate* solution ($> 99\%$) good results were obtained in ammoniacal tartrate solution containing excess potassium cyanide. The maximum density value was normal (exp. 31).

In *lead nitrate* solution with ammoniacal citrate, no end-point was reached and the density increased after the calculated end-point had been reached (exp. 32). In ammoniacal Na_2H_2EDTA the titration could be carried out successfully. Although the initial precipitation occurred very late, the maximum density value was normal (exp. 33).

In *copper nitrate* solutions the determination could be made neither in ammoniacal citrate solution which contained much larger amounts of potassium cyanide, nor in ammoniacal Na_2H_2EDTA. In both cases the density rose after the calculated end-point had been reached. The same negative results were obtained in the presence of $SbCl_3$ or antimonate with all complexing agents. The titrations were successful in solutions containing *mercuric nitrate* ($> 99\%$), or *silver nitrate* ($\sim 98\%$) if these solutions contained excesses of potassium cyanide in addition to the ammoniacal tartrate. The density was normal in both cases (exps. 34 and 35).

SUMMARY

The reaction between bismuth(III) and sodium diethyldithiocarbamate was investigated. The conditions necessary for the heterometric determination of small amounts of bismuth in other metals were studied. Various complexing agents were used. Methods and conditions are presented for the direct determination of bismuth ($\sim 2\%$) in salts of the following cations: Ca^{+2}, Ba^{+2}, Mg^{+2}, Zn^{+2}, Mn^{+2}, Co^{+2}, Ni^{+2}, Al^{+3}, Cr^{+3}, Fe^{+3}, Cd^{+2}, Pb^{+2}, Hg^{+2} and Ag^{+}. A titration lasted 10-15 minutes, and the error in most cases was close to zero.

RÉSUMÉ

Les auteurs ont étudié la réaction qui se passe entre le bismuth(III) et le diéthyldithiocarbamate de sodium, ainsi que les conditions nécessaires pour le dosage hétérométrique de faibles quantités de bismuth en présence d'autres métaux. Différents réactifs complexants ont été utilisés. Des méthodes et des conditions sont proposées pour le dosage direct du bismuth ($\sim 2\%$) dans les sels des cations suivants: Ca^{+2}, Ba^{+2}, Mg^{+2}, Zn^{+2}, Mn^{+2}, Co^{+2}, Ni^{+2}, Al^{+3}, Cr^{+3}, Fe^{+3}, Cd^{+2}, Pb^{+2}, Hg^{+2} et Ag^{+}. Un titrage dure 10-15 minutes; l'erreur est, dans la plupart des cas, presque nulle.

ZUSAMMENFASSUNG

Die Reaktion zwischen Wismuth(III) und Natriumdiäthyldithiocarbamat wurde untersucht. Die Bedingungen für die heterometrische Bestimmung von kleinen Mengen Wismuth in anderen Metallen wurden in den einzelnen Fällen festgelegt. Verschiedene Komplexbildner wurden angewandt. Methoden und Bedingungen für die direkte Bestimmung von Wismuth in Salzen der folgenden Kationen wurden angegeben: Ca^{+2}, Ba^{+2}, Mg^{+2}, Zn^{+2}, Mn^{+2}, Co^{+2}, Ni^{+2}, Al^{+3}, Cr^{+3}, Fe^{+3}, Cd^{+2}, Pb^{+2}, Hg^{+2}, Ag^{+}. Eine Titration dauert 10-15 Minuten und der Fehler is meistens beinahe Null.

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DIFFUSION COEFFICIENTS AT ROTATED MICROELECTRODES

by

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The applicability of rotated electrodes in voltammetric investigations and amperometric titrations has warranted numerous studies concerning their behavior in various chemical systems. While several fundamental studies[1–3] have considered the various factors, such as angular velocity and area of the electrode and concentration and diffusion coefficient of the electroactive species, which influence the limiting current at a rotated solid electrode, few experimental results have confirmed these theories. For instance, it is now recognized that there is no unique relation between limiting current and angular velocity independent of the nature of the electrode process. The apparent discrepancies between experiment and theory result largely because the electrodes commonly employed do not have geometrical shapes which lend themselves to theoretical treatment.

Because of the irreproducible nature of solid surfaces, the major applications of rotated electrodes involve comparison of the limiting currents for various electrode reactions. The linear relation between limiting current and concentration for a single electrode reaction is well established, but to intercompare different electrode reactions, it is necessary to know also the relation between limiting current and diffusion coefficient since the transport of matter to a rotated electrode is not entirely by diffusion but is partially by convection. At constant angular velocity, the limiting current i_1 at a rotated electrode is given by

$$i_1 = knCD^a \quad \ldots\ldots\ldots\ldots \quad (1)$$

or

$$\log \frac{i_1}{nC} = k' + a \log D \quad \ldots\ldots\ldots\ldots \quad (2)$$

where n is the number of electrons involved in the electrode reaction, C is the concentration and D the diffusion coefficient of the electroactive species. Plotting $\log i_1/nC$ against $\log D$, the dependence of the limiting current upon the diffusion coefficient is given by the slope a. The ordinate intercept k' is proportional to the electrode area. Contrary to FERRET AND PHILLIPS[4], the slope is sufficiently sensitive to distinguish between $a = 3/4, 1/2, 1/3$, etc.

EXPERIMENTAL

C. P. chemicals and conductivity water were used to prepare all solutions. Dichlorocuprate (I) was prepared by reducing a standard copper (II) sulfate solution with fine copper wire in 6*M* hydrochloric acid. Limiting currents for each electrode reaction were measured, using a manual polarograph[5], at two or three concentrations to verify linearity between limiting current and concentration.

Platinum electrodes were prepared by sealing a short length (*ca.* 1/2 inch) of 18 gauge wire coaxially into the end of a 10-inch length of soft glass tubing. Electrical connection was provided by filling the tube with mercury. The electrode assembly was placed in a chuck and rotated about the axis of the electrode at 600 r.p.m. with a synchronous motor. Transport involving laminar flow to a rotated cylinder electrode has been treated theoretically (*vide infra*), whereas the more common electrode in which the wire is sealed perpendicular to the axis of the tubing[4] introduces turbulence and cannot be so treated. FERRET AND PHILLIPS[4] have recently described waxing the trailing edge of a "perpendicular" electrode to prevent turbulent convection thus giving well defined current-potential curves.

The sensitivity, $k_{\rm ion}$, of an electrode rotated at constant angular velocity is defined as the magnitude of the limiting current observed for the given electrode reaction divided by the bulk concentration of the electroactive species and is proportional to the area of the electrode. The electrodes used in this study exhibited sensitivities of (A) 269 and (B) 116 μa/mmole/l for the reduction of silver(I).

DISCUSSION

Limiting currents were measured at two rotated platinum electrodes for five ionic species in 0.1 M potassium nitrate, in 0.1 M sodium perchlorate, and in 0.1 M potassium chloride; in addition, silver(I) and hexacyanoferrate(II) and (III) were measured in potassium nitrate and sodium perchlorate, and dichlorocuprate(I) was measured in potassium chloride. The diffusion coefficients at infinite dilution, D°, were calculated from the limiting ionic equivalent conductances[6] using the Nernst expression. The diffusion coefficient for dichlorocuprate(I) was determined by comparison with that for copper(II) in 0.1 M potassium nitrate and in 0.1 M potassium chloride at the dropping mercury electrode using the Lingane-Loveridge equation and was calculated to be $1.21 \cdot 10^{-5}$ cm^2/sec. This value agrees well with that for analogous univalent ions. The plots of log i_1/nC against log D° for the two electrodes and various ionic species are shown in Fig. 1. Lines with slope 0.67 are fitted through the points for each electrode, and except for the ionic species of copper(II) and hexacyanoferrate(II) and (III), the

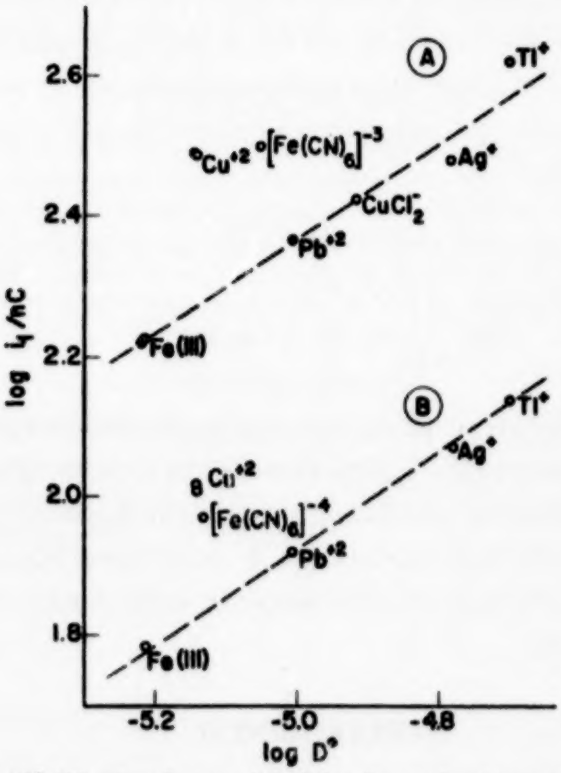

Fig. 1. Log i_1/nC versus log D^0. Electrode sensitivities for reduction of silver(I): (A) 269 μa/mmole/l; (B) 116 μa/mmole/l.

limiting current is observed to vary with the two-thirds power of the diffusion coefficient. The two-thirds power relation agrees with that predicted for laminar flow by LEVICH[1] at a rotated disc electrode, by TACHI *et al.*[2] at a rotated cylinder microelectrode, by EISENBERG *et al.*[3] at a rotated cylinder electrode of large area (60 to 240 cm^2), and by LIN *et al.*[7] at a stationary cylinder cathode.

The apparent agreement between experiment and theory deserves consideration, however. The diffusion coefficient of the iron(III) is calculated from the limiting equivalent conductance of the Fe^{+3} ion, whereas the principal ionic species in nitrate and perchloric media probably is $Fe(OH)^{+2}$ [8], the diffusion coefficient of which is unknown. In 0.1M potassium chloride, the ionic species of copper(II), lead(II), and iron(III) apparently are the same as in nitrate and perchlorate media inasmuch as similar i_1/nC values are observed; complexing sufficient to change the average charge of the species should result in different i_1/nC values. The voltammetrically reversible silver(I)-(O) couple[5] and the irreversible iron(II)-(III) couple[9] obey the two-thirds power relation. The failure of copper(II) and the reversible hexacyanoferrate(II) and (III) to exhibit this relation is not obvious. Recent discussions concerning the relations between the electronic configuration of the electroactive species and the nature of the electrode process[10,11] do not correlate these observations.

Comparison of the limiting currents for different electrode reactions tacitly assumes that the ratio of the diffusion coefficients of the various electroactive species at constant ionic strength is equal to that at infinite dilution. This approximation is not rigorous and partially may account for the deviations observed in Fig. 1, especially for the highly charged hexacyanoferrate(II) and (III) species. GOKSHTEYN[12] estimates that the diffusion coefficients used in the Ilkovich equation are, on the average, about 23% too large. JORDAN[13] reports that diffusion coefficients calculated from the Ilkovich equation are 10 to 25% larger than those calculated using the Lingane-Loveridge equation. SANDBORN AND ORLEMANN[14] have measured the diffusion coefficient of nickel(II) at two ionic strengths using a capillary technique. The ratio of the diffusion coefficient at given ionic strength to that at infinite dilution, $D/D°$, is 0.87 and 0.78 at ionic strengths of approximately 0.1 and 3.0 respectively. Using a similar capillary technique, EISENBERG *et al.*[3] report $D/D°$ values of 0.53 for hexacyanoferrate(II) and 0.51 for hexacyanoferrate(III) at ionic strengths of 4.0 and 3.2 respectively. While these latter ratios are probably too small, it seems clear that there is considerable variation in diffusion coefficient with ionic strength for the different electroactive species; there is no reason to expect otherwise. Probably the best method for estimating diffusion coefficient under conditions similar to those extant in voltammetry is that of an electrode reaction with only linear diffusion as employed by LAITINEN AND KOLTHOFF[15]. While their data indicate values for $D/D°$ of about 0.97 for silver(I) and hexacyanoferrate(II) and (III) at ionic strength 0.12 to 0.15, the concentration of inert electrolyte never exceeded twenty times that of the electroactive species, and these ratios probably are somewhat large. Refined measurements of this type are urgently needed for voltammetric studies.

SUMMARY

The limiting current for several electrode reactions at a rotated microelectrode is observed to vary with the two-thirds power of the diffusion coefficient at infinite dilution in accordance with the theories of TACHI, EISENBERG, LIN, and others. However, the uncertainties involved in estimating

diffusion coefficients at given ionic strength require, that for accurate work, the limiting currents for different electrode reactions be compared on the basis of *electrode sensitivity*, $k_{\text{ion}} = i_1/C$, and without regard to the role of diffusion in the transport process. The method of LAITINEN AND KOLTHOFF using an electrode reaction with only linear diffusion is recommended for measuring diffusion coefficients at given ionic strength under conditions similar to those extant in voltammetry.

RÉSUMÉ

Le courant limite de plusieurs réactions aux électrodes, dans le cas d'une microélectrode rotative, varie avec la puissance 2/3 du coefficient de diffusion, pour une dilution infinie, conformément aux théories de TACHI, EISENBERG, LIN, etc. Cependant, lors de l'estimation des coefficients de diffusion pour une force ionique donnée, il est nécessaire, pour un travail précis, de comparer les courants limites de différentes réactions d'électrode sur la base de la sensibilité d'électrode $k_{\text{ion}} = i_1/C$, sans tenir compte du rôle de la diffusion dans le processus de transport. La méthode de LAITINEN ET DE KOLTHOFF utilisant une réaction d'électrode, avec une diffusion linéaire seulement, est recommandée pour la mesure des coefficients de diffusion à force ionique donnée, dans des conditions semblables à celles de la voltammétrie.

ZUSAMMENFASSUNG

Es wurde beobachtet dass der Grenzstrom für verschiedene Elektrodenreaktionen an einer rotierenden Mikroelektrode mit der 2/3 Potenz des Diffusionskoeffizienten bei unendlicher Verdünnung gemäss den Theorien von TACHI, EISENBERG, LIN und anderen variiert. Aber die Ungenauigkeit der Bestimmung von Diffusionskoeffizienten bei gegebener Ionenstärke macht es nötig, dass bei genauen Arbeiten die Grenzströme für verschiedene Elektrodenreaktionen auf Grund der Elektrodenempfindlichkeit $k_{\text{ion}} = i_1/C$ verglichen werden und zwar ohne Berücksichtigung der Rolle, die die Diffusion bei dem Transportprozess spielt. Die Methode von LAITINEN UND KOLTHOFF die zur Messung von Diffusionskoeffizienten bei gegebener Ionenstärke unter ähnlichen Bedingungen wie in der Voltammetrie eine Elektrodenreaktion mit nur lineärer Diffusion verwendet, wird empfohlen.

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ESTIMATION OF TUNGSTATE ION BY TENSAMMETRY

by

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PROSKURNIN AND FRUMKIN[1] and GRAHAME[2] observed capacitance peaks when surface active substances were adsorbed at the metal/solution interface of a mercury electrode; the measurements were carried out by superposing a small, low frequency alternating voltage onto the direct potential applied to the electrode. Their method, however, is tedious because it involves current balancing at each value of the applied direct potential.

In 1951 it was shown by BREYER[3] and in the following year by BREYER AND HACOBIAN[4] and by DOSS AND GUPTA[5] that the alternating current polarographic method[6–8] can be used with advantage for this type of investigation. Here, the alternating current is directly read from a meter and its value plotted against the applied direct potential. Wave shaped current-voltage curves are thus obtained which have their origin in adsorption/desorption processes occurring at the electrode. To distinguish this type of process from alternating current polarography, a new term "tensammetry" has been coined.

It is the object of this communication to show that tungstate ion also produces tensammetric waves which can be used for the quantitative estimation of that ion.

EXPERIMENTAL

All chemicals used were of analytical grade.

The apparatus, which is shown in Fig. 1, can be constructed from readily available commercial instruments. A small sinusoidal voltage of about 0.015 V r.m.s. (root-mean-square) is superimposed onto the direct potential E, derived from an accurate potentiometer P, whose total resistance should not exceed 40 ohms. In order to keep the impedance of the cell circuit low, a condenser C of about 100 μF is inserted between the reference electrode R and the mercury pool in the cell. The cell current passes through the resistance r_3 and the potential drop across it is applied to the input of a conventional three stage microphone amplifier, having a gain of about 10.000. The output is connected to an ordinary a.c. voltmeter having a sensitivity of 2.5 V for full scale deflection. In order to evaluate the current flowing through the cell, the meter is initially standardized by substituting fixed resistors of known values for the cell assembly. The sensitivity is conveniently adjusted by means of the amplifier gain control. The actual analysis is carried out by plotting the value of the alternating current flowing through the cell against the applied direct potential and measuring the height of the resulting wave. Proper shielding of all cell leads is essential.

RESULTS

Fig. 2 shows the tensammetric waves produced by sodium tungstate in a 0.1 M phosphate-acetate-borate buffer of pH 1.8 (PRIDEAUX AND WARD[9]). Essentially two

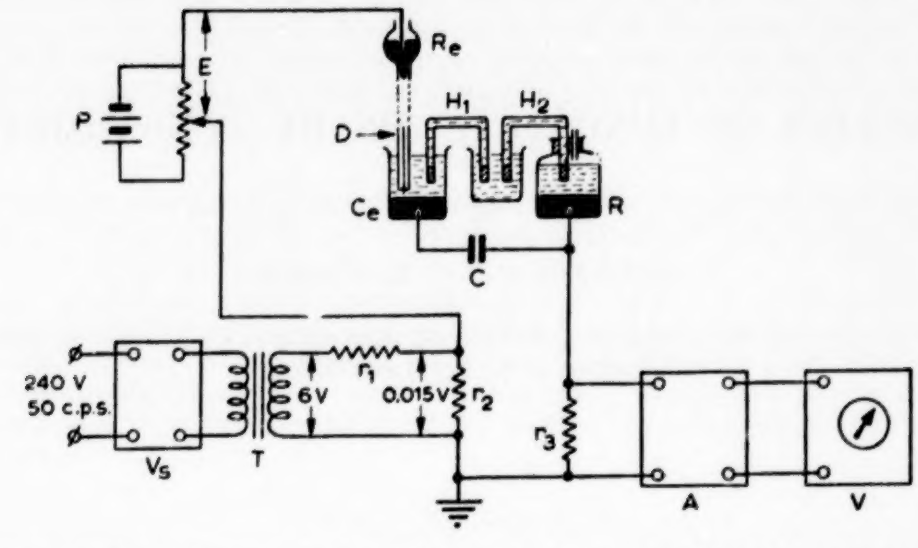

Fig. 1. Schematic representation of the apparatus used. A, amplifier (5 watt output); C, 100 μF condenser; C_e, polarographic cell with mercury pool; D, dropping mercury electrode; H_1 and H_2, salt bridges; P, potentiometer; R, reference electrode; r_1, resistor, 400 ohm, ½ watt; r_2, resistor, 1 ohm, ½ watt; r_3, resistor, 25 ohm, ½ watt; R_e, mercury reservoir; T, step down transformer, 6 V output; V, a.c. voltmeter, sensitivity 2.5 V for full scale deflection; V_s, magnetic voltage stabilizer.

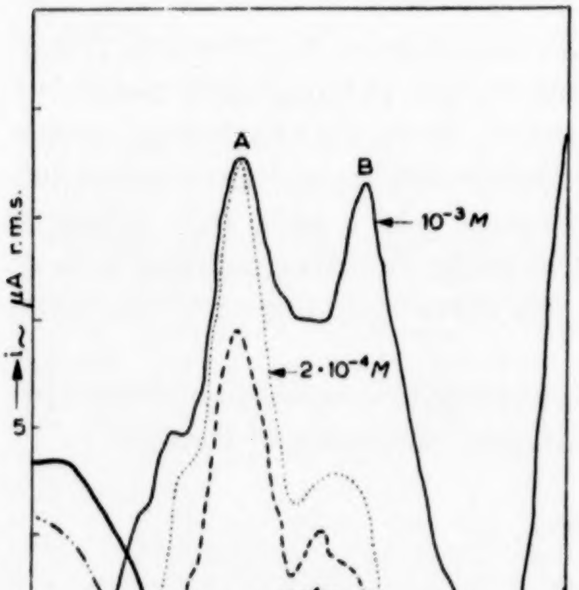

Fig. 2. Tensammetric waves at varying concentrations of Na_2WO_4 in 0.1*M* phosphate-borate-acetate buffer pH 1.8; superposed alternating voltage 0.015 V r.m.s.; T = 20°C.

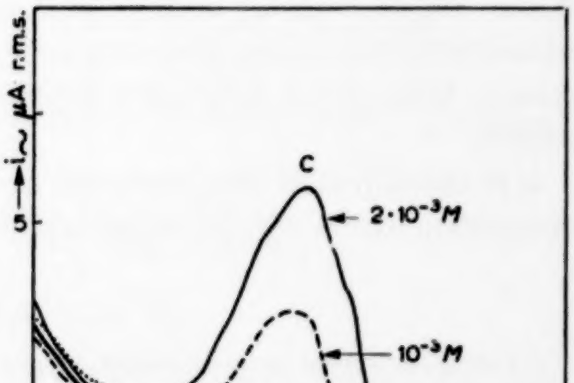

Fig. 3. Tensammetric waves of Na_2WO_4 in 0.1*M* phosphate-borate-acetate buffer pH 4; superposed alternating voltage 0.015 V r.m.s.; T = 20°C.

References p. 500

waves are obtained, wave A at approximately —0.4 V and wave B at about —0.64 V (*versus* the saturated calomel electrode). At low tungstate concentrations only wave A appears. Both waves reach a limiting value at higher concentrations of tungstate (10^{-3} to $2 \cdot 10^{-3}M$). Good waves are also obtained in a mixture of $0.5M$ $NaClO_4$ and $0.1M$ $HClO_4$ as supporting electrolyte.

At pH 4 only one wave is obtained (wave C, Fig. 3) but its magnitude is considerably less than those of waves A and B. At pH values higher than 6 no tensammetric waves appear. It seems reasonable to assume, therefore, that the surface active compound responsible for the production of tensammetric waves is not the WO_4^{-2} ion but rather a form which is stable in acid solutions, such as HWO_4^- ion, tungstic acid, or their polymers. In the case of buffers containing phosphate and/or borate as supporting electrolyte, complexes formed with tungstate ion would also have to be considered as a possible source for the production of tensammetric waves. This aspect of the work is at present under investigation.

Fig. 4 shows that the calibration curve for wave A rises rapidly within the concentration range between $2 \cdot 10^{-5}$ and $2 \cdot 10^{-4}M$ Na_2WO_4. It is, however, possible to extend the useful analytical range up to a concentration of $10^{-3}M$ by making use of the calibration curves obtained either from wave B or C.

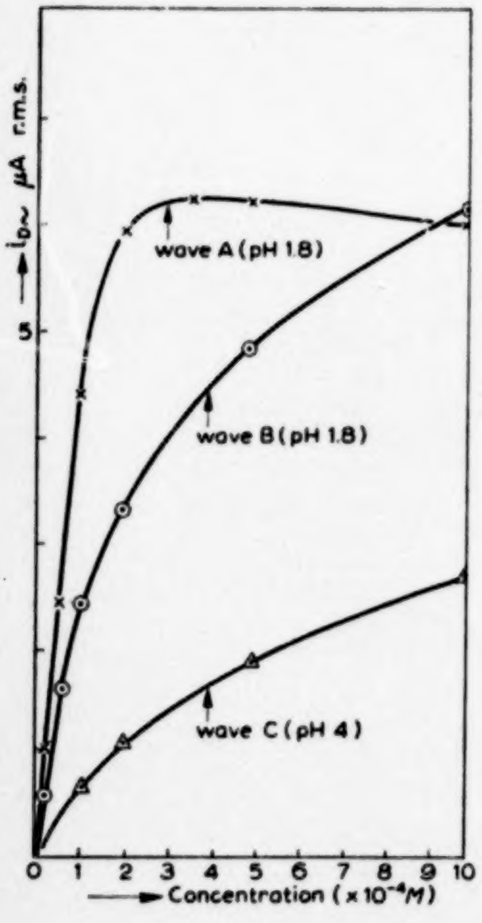

Fig. 4. Calibration curves of Na_2WO_4 in $0.1M$ phosphate-borate-acetate buffer.

SUMMARY

It is shown that tungstate ion can be estimated quantitatively by the same experimental technique as that used for alternating current polarography. The underlying process differs, however, fundamentally from polarography in that no electron transfer takes place at the electrode and thus no d.c. polarographic steps are obtained. The alternating current is produced solely by adsorption/desorption processes at the electrode/solution interface, a phenomenon to which the name "tensammetry" has been given.

The current-voltage curve for sodium tungstate at pH 1.8 shows two well defined tensammetric waves which can be used for purposes of quantitative estimation. No waves are obtained at pH values higher than 6, showing that the compound responsible for the production of the waves is not the simple WO_4^{-2} ion.

RÉSUMÉ

L'anion tungstique peut être dosé quantitativement par la même technique que celle utilisée pour la polarographie, à courant alternatif. La méthode proposée diffère cependant de la polarographie par le fait qu'il n'y a pas de transfert d'électrons à l'électrode et qu'on n'obtient pas de paliers polarographiques de courant direct. Le courant alternatif n'est produit que par des processus d'adsorption/désorption à la surface électrode/solution; le nom de "tensammétrie" a été donné à ce phénomène. La courbe courant-voltage pour le tungstate de sodium au pH 1.8 présente deux vagues "tensammétriques" bien définies, pouvant servir à une analyse quantitative. Aucune vague n'est obtenue à un pH supérieur à 6, ce qui prouve que l'ion donnant les vagues n'est pas le simple WO_4^{-2}.

ZUSAMMENFASSUNG

Es wird gezeigt, dass das Wolframation quantitativ mit Hilfe derselben Versuchstechnik bestimmt werden kann, wie sie bei der Wechselstrompolarographie verwendet wird. Der Prozess der dieser Bestimmung zugrunde liegt, unterscheidet sich aber wesentlich dadurch von der Polarographie, dass kein Elektronentransport an der Elektrode stattfindet und dass man also keine polarographischen Gleichstrom-Stufen erhält. Der Wechselstrom wird nur durch Adsorptions-Desorptions-Vorgänge an der Kontaktfläche von Elektrode und Lösung bewirkt; diese Erscheinung wurde "Tensammetrie" genannt. Die Strom-Spannungs-Kurve für Natriumwolframat bei pH 1.8 zeigt zwei deutliche tensammetrische Wellen die zur quantitativen Bestimmung benützt werden können. Bei pH-Werten die höher als 6 liegen, erhält man keine Wellen, woraus sich ergibt, dass die für die Wellen verantwortliche Verbindung nicht das einfache WO_4^{-2}-Ion ist.

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AN ASSESSMENT OF THE STABILITY DATA OF METAL CHELATE COMPOUNDS WITH SPECIAL REFERENCE TO ANALYTICAL CHEMISTRY

by

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During the past ten years a large amount of data on the stabilities of metal complexes has accumulated and many of them are of considerable analytical interest. It seems propitious at this time to assess these data; this will be done by reference to the work on the metal chelates of 8-hydroxyquinoline and related compounds which are so often used in analytical chemistry.

The potentiometric (pH meter) method of BJERRUM[1] and its wider application due to CALVIN AND WILSON[2] are well known. The following points of experimental and theoretical importance should be noted.

The practical procedure is essentially very simple and usually involves metal and complexing agent concentrations of $\sim 10^{-3} M$. As a result determinations at pH < 3 are liable to considerable errors assuming that the pH meter is accurate to ± 0.02 unit. Thus in the copper-picolinic acid system, at pH 2.44, the degree of formation** $\bar{n} = 1.21$, but if the meter had read 2.46, $\bar{n} = 1.05$. FREISER, CHARLES AND JOHNSTON[3] have shown also that at pH > 7, there is a source of error in hydrolysis. These discrepancies usually manifest themselves in the lack of symmetry of the formation curves[4], obtained by plotting $\bar{n}$ against the log of the free ligand concentration. In addition it is necessary that the dissociation exponents of the parent compound from which the ligand is derived should be known, if possible under the same conditions as $\bar{n}$. If any of these pK's are less than 3, its measurement can involve much difficulty and if chelation takes place at pH < 3.5 the effect of any error in the value of pK will be considerable.

In practice the insolubility of the chelates in aqueous solution makes it necessary for the systems to be studied in mixed organic solvents, usually dioxan-water. There are clearly great difficulties in interpreting the measurements with the glass-electrode in such solvents. Thus it would be virtually impossible to determine thermodynamic constants and stoichiometric constants could only be calculated after carrying out some sort of calibration of the electrode system.

Referring briefly to the mathematical analysis involved it is to be noted that the simple and commonly used graphical method of calculation [in which the values of log

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** The degree of formation, $\bar{n}$, is defined by

$$\bar{n} = (T_A) - (A)/(T_M),$$

where (T_A) and (T_M) are the total concentrations of metal and ligand respectively and (A) the concentration of free ligand.

(concentration of free ligand) at $n = 1, {}^1/_2, 1{}^1/_2$ gives logs of K, k_1 and k_2 respectively, $K = (k_1k_2)^{1/2}$] can be used only when $\log k_1 - \log k_2 \geqslant 2.5$[5]. This particular figure applies to bis-complexes only and although it is readily extended to the systems having higher coordination, attention will be confined here to the more commonly occurring complexes in analytical chemistry having a coordination number of 2. When the above condition is not satisfied the equation (i) should be employed, either graphically or statistically,

$$n/(1 - n)(A) = k_1 + k_1k_2(2 - \bar{n})(A)/(1 - \bar{n}) \quad \ldots\ldots\ldots\ldots\ldots \text{(i)}$$

where (A) = free ligand concentration and k_1 and k_2 as elsewhere in this paper are the stoichiometric formation constants for a bis-complex.

It is now possible to consider the data recorded in Table I ($\delta\log k = \log k_1 - \log k_2$). The experimental background of these figures can be summarised: those of Johnston and Freiser[6] were obtained in 50% dioxan-water and calculated using the simple graphical method and with a partial correction for working in the mixed aqueous solvent; the data of Irving and Rossotti[7] and those by Holmes and Crimmin[8,9] quoted here were also determined in 50% dioxan-water and attempts made to correct for the solvent effect and calculated using (i). These studies can be looked upon in one way as

TABLE 1

Chelating compound		*Cu*	*Ni*	*Co*	*Zn*	*Mg*	*H*
8-Hydroxy-	[6] $\log k_1$	13.49	11.44	10.55	9.96	—	3.97
quinoline	$\log k_2$	12.73	9.94	9.11	8.90	—	11.54
	$\delta\log k$	0.76	1.50	1.44	1.06	—	
	[7] $\log k_1$	13.03	10.43	—	9.34	5.04	4.48
	$\log k_2$	12.35	9.97	—	8.22	4.29	10.80
	$\delta\log k$	0.68	0.46	—	1.12	0.75	
2-Methyl-	[6] $\log k_1$	13.00	9.50	9.68	10.10	—	4.51
8-hydroxy-	$\log k_2$	11.64	8.50	8.92	9.07	—	11.69
quinoline	$\delta\log k$	1.36	1.00	0.76	1.03	—	
	[7] $\log k_1$	10.22	8.52	—	8.66	3.73	5.01
	$\log k_2$	9.32	7.96	—	8.10	3.13	11.01
	$\delta\log k$	0.90	0.56	—	0.56	0.60	
8-Hydroxy-	[7] $\log k_1$	10.56	—	—	7.48	3.89	3.30
quinazoline	$\log k_2$	9.54	—	—	6.96	2.91	9.59
	$\delta\log k$	1.02	—	—	0.52	0.98	
2,4-Dimethyl-	[7] $\log k_1$	10.26	7.88	—	7.77	3.81	3.15
8-hydroxy-	$\log k_2$	9.74	7.00	—	7.01	3.09	10.14
quinazoline	$\delta\log k$	0.52	0.88	—	0.76	0.72	
Picolinic	[8] $\log k_1$	6.33	5.78	5.70[9]	—	—	1.5
acid	$\log k_2$	5.91	5.62	5.66	—	—	5.43
	$\delta\log k$	0.42	0.16	0.04	—	—	(1.5)[9]
							(5.71)
6-Methyl	[8] $\log k_1$	6.34	4.87	4.14	—	—	0.9
picolinic	$\log k_2$	6.03	4.39	3.90	—	—	5.77
acid	$\delta\log k$	0.31	0.48	0.24	—	—	(1)[9]
							(6.59)

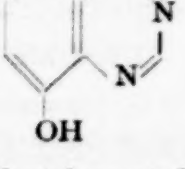
Note. For the purposes of convenience in this table, $\log k_1$ and $\log k_2$ for the H-complex are equated to pK_1 and pK_2 respectively and the figures in parentheses are the dissociation exponents of the acids indicated but in different solvents.

following up the observation of MERRITT AND WALKER[10] on the effect of steric hindrance due to the methyl group in preventing the precipitation of the Al^{+3} complex of 2-methyl-8-hydroxyquinoline (2-methyloxine). The data here should give a clearer insight into the utility of the steric factor in analytical chemistry.

After the first ligand has been attached to the cation, the ease with which the next molecule is coordinated to this ion is reflected in the spread of the formation constants. Thus other things, such as the pK's of the parent acids, HA, being equal, one would expect log K of a sterically hindered complex to be less than that of one formed without pronounced steric hindrance. Since the substitution of the group which hinders with respect to the parent chelating agent usually changes the pK's, the interpretation of the results might not be straightforward, but the value of $\delta \log k$ should not be as dependent as log K upon this change in the dissociation exponents of the acid HA.

In spite of the rather adverse comments made above on the data of JOHNSTON *et al.*[6] the following points may be fairly made. Thus, as one would expect, the stabilities of the 2-methyloxinates are lower than those of the corresponding oxinates. In addition, in the case of the Cu, Zn and Co, complexes, $\delta \log k$ is less for the oxinates than for the 2-methyloxine chelates. This is as one would predict and so is the particularly large increase in the value of $\delta \log k$ for the Cu-complex of 2-methyloxine in view of the planar structure of the Cu chelates. On the other hand, the value of $\delta \log k$ for Ni oxinate is greater than that for the corresponding 2-methyloxinate and this is especially significant when one recalls that the Ni chelates are also usually planar. The seemingly anomalous value of this system could not be expected to be reversed by using the more refined method of calculation previously mentioned.

Referring now to the comprehensive data of IRVING *et al.*[7], it is seen that the value of $\delta \log k$ for the Cu and Ni chelates of 2-methyloxine is greater than in the case of the oxinates. There is, however, a significant drop in this spread on going from the Zn-complex of oxine to that of the 2-substituted complex. In the case of the complexes formed with 8-hydroxyquinazoline



they would be expected to be somewhat less stable than those formed with 2,4-dimethyl-8-hydroxyquinazoline on account of the lower value of pK_a. In actual fact the stabilities are almost equal and this could be attributed to the blocking effect of the 2-methyl group. As has already been pointed out, this effect should be more evident in the case of the planar Cu and Ni chelates but this is seemingly not so. Thus in the Cu-complex, $\delta \log k$ is 0.52 for the 2,4-dimethyl-8-hydroxyquinazolinate and 1.02 for the 8-hydroxyquinazolinate. One possible explanation of this result is the effect on the spread of the differences in the dissociation exponents of the hydrogen-ligand complexes. That is, the increased overall stability of the chelates of the 2,4-dimethyl derivatives could be expected to lessen the steric effect of the methyl group at position 2. In the case of the oxinates and 2-methyloxinates however, although the latter should, as far as the values of the dissociation exponents are concerned, have slightly higher stability constants, log K for Cu oxinate is some 6 units greater than the corresponding 2-methyloxinate. It would seem then, that steric effects are more important than the values of the pK's of the chelating agents in deciding both overall stability and the value of $\delta \log k$, at least for ligands which are as similar as the ones under consideration. On the basis of this reasoning, it is difficult to explain the fact that $\delta \log k$ is less for the Cu complex of 2,4-dimethyl-8-hydroxyquinazoline than for the un-substituted 8-hydroxyquinazoline. Further, 2-methyloxine has pK's which are higher than those for 2,4-dimethyl-8-hydroxyquinazoline and the complexes formed with it should be correspondingly stabler, but this does not seem to be the case.

With respect to the data of HOLMES *et al.*[8,9] there seems to be the same evidence for the steric effect of substituents in positions similar to that occupied by the methyl group in 2-methyloxine. Thus in the case of the Ni complexes of picolinic acid and 6-methylpicolinic acid, the value of $\delta \log k$ is greater for the latter, while the overall stability is less, even though the pK's for the 6-methyl compound are higher. The case of the Cu chelates of these two acids seems to present the same sort of anomaly as that noted in the work of IRVING *et al.*

In the light of the above discussion there is some general agreement in the results of various workers but there are also several seeming contradictions on comparing different sets of data and also inconsistencies within the work of individual authors. These anomalies cannot be explained away and since in addition to the problem of steric hindrance stability data are of critical importance in, for example, discussions of precipitation and solvent extraction, the results of the potentiometric method should not be pressed too far. It would seem that the experimental results are in conflict mainly because of the inherent difficulties in the method. As yet, the most important method in the search for improved reagents is still chemical intuition based on experience.

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SUMMARY

An evaluation of the results of the potentiometric method of determining stability data is presented in the light of illustrations of importance in analytical chemistry.

RÉSUMÉ

L'auteur fait un exposé sur la valeur de la détermination potentiométrique de la constante de stabilité des complexes, en prenant comme exemple des cas intéressant la chimie analytique.

ZUSAMMENFASSUNG

Der Wert der potentiometrischen Methode zur Bestimmung der Stabilität von Komplexen wird an Hand von Beispielen die für die analytische Chemie von Bedeutung sind, erörtert.

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A SIMPLIFIED SEPARATORY FUNNEL FOR USE IN LIQUID AMALGAM REDUCTIONS

by

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Liquid amalgams such as Pb, Bi, Cd, Sn and Zn, have been shown to be valuable reductants as preparational analytical reagents both for pre-reduction of standard solutions and for quantitative reductions and removal of excess reductant preparatory the determination of unknown components in solutions thus pretreated.

Neither of these analytical applications for liquid metal amalgams has attained much practical acceptance because, among other reasons, the quantitative separation of solutions or samples for analysis from the liquid amalgam, a liquid-liquid two phase system, has presented too much of a problem.

The present work has for its objective the description of a new type separatory funnel, which, while simple in design, readily simplifies amalgam reductions in successfully providing a practical procedure and device for the facile quantitative partition of aqueous and amalgam liquid phases. It may be employed for the reduction of samples for analysis but is most valuable as a tool in the preparation and storage of reducing agents such as ferrous, vanadyl and titanous solutions as are frequently used as volumetric standard reagents.

PREPARATION AND PHYSICAL-ELECTROCHEMICAL REDUCTION POTENTIALS OF COMMONLY EMPLOYED LIQUID AMALGAMS

The reduction potentials, commonly involved in the prepared liquid amalgams are as follows:

$$
\begin{array}{llll}
BiO^{+} + 2H^{+} + 2e & \rightarrow & Bi + H_2O & 0.32 \text{ volts} \\
Pb^{+2} + 2e & \rightarrow & Pb & -0.126 \text{ ,,} \\
Sn^{+2} + 2e & \rightarrow & Sn & -0.136 \text{ ,,} \\
Cd^{+2} + 2e & \rightarrow & Cd & -0.402 \text{ ,,} \\
Zn^{+2} + 2e & \rightarrow & Zn & -0.762 \text{ ,,}
\end{array}
$$

The amalgam is generally 5 percent of the above listed metals and procedures for their preparation[1] are of marked simplicity. For example a 200 g sample of pure mercury is placed in a 250 ml beaker. 10 g of millet seed size zinc is added. Approximately 0.5 ml of concentrated hydrochloric acid is added to clean the surface of the zinc granules. Stir the mixture to promote the almost instantaneous dissolution of zinc in mercury. Finally wash the resulting amalgam with dilute acid and strain the liquid amalgam through a fine texture cotton cloth and store the product under a 1 percent solution of hydrochloric or sulfuric acids in a 100 ml glass bottle.

PREVIOUS STUDIES

A comprehensive recording of the previously published work dealing with the study of applications employing liquid amalgams in analysis is not appropriate in connection with the present discussion. Brief reference only will be made here to particular topics. A series of papers were contributed by SOMEYA[1] and by NAKAZONO[2]. The former observer has devised a suitable separatory funnel for carrying out liquid amalgam reductions with provision for the satisfactory separation of the resulting amalgam from the aqueous solution reduced. This apparatus provided for titration of the reduced element for subsequent determination by standard oxidant, with or without contact with atmospheric oxygen. The manipulative details in its use are somewhat involved and prospective users, seemingly found the procedures thus impaired, beyond popular exceptance. This detail resulted in the more convenient use of solid amalgamated zinc[3], (the familiar JONES reductor), substitution. The more recent use of the WALDEN silver reductor[4] of less intense reduction potential, has been popular for reactions requiring only a lesser reduction intensity but must employ hydrochloric acid to alter the otherwise higher voltage magnitude.

Other means have been provided[5] which simplify the practical manipulations for the use of liquid amalgams as a great improvement over the use of the SOMEYA[1] apparatus. Fused Wood's metal has been applied[6] to substitute for liquid amalgams. The applications in the use of the JONES reductor are outlined by LUNDELL AND HOFFMAN[7] and the same reactions are provided in the use of the zinc amalgam under duplicate conditions.

Employing the LUNDELL AND HOFFMAN classification of the elements according to atomic number the use of a liquid zinc amalgam (or the JONES reductor), the metal ions reduced are shown in Table I.

TABLE I

REDUCTION BY ZINC AMALGAM IN 5 + 100 REAGENT SULFURIC ACID

Designation outer shell														*Number of electrons in completed outer shells* K, L, M, N, O, P, Q
N	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	2, 8, 18, 8
O		Cb	Mo		Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	2, 8, 18, 18, 8
P			W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	2, 8, 18, 32, 18, 8
Q			U											2, 8, 18, 32, 18, 12, 2

The outer shell designation periods N, O, and P terminate when complete in Kr, Xe, and Rn.
Elements in solid blocks are reduced to definite valences, and in solid broken blocks are reduced to indefinite valences.
Light blocks enclose elements reduced to metals.
Carbon and nitrogen compounds of the L period (not included in Table I) are reduced to indefinite valences (for example nitrates).

By critical examination of the schematic classification (Table I), the great advantage attained in the use of Pb, Bi, Cd, and Sn amalgams is at once apparent. The use of zinc amalgam does not provide for the reduction of Fe(III) without also reducing Ti(IV) to Ti(III). A bismuth liquid amalgam can be used for preferential reduction of iron in the presence of titanium. Chromium (valence states 6, 3, and 2), is reduced by zinc amalgam (or the JONES reductor), to its lowest valence while Bi, Pb, and Sn amalgams carry the reduction only to the trivalent state. Molybdenum (valence states 6, 5, and 3), presents a comparable situation. If a nitrate present is reduced by the use of a zinc amalgam it is obviously preferable to employ a lead amalgam. The troublesome formation of gas due to the presence of arsenic or antimony when a zinc or cadmium amalgam is employed may be prevented by the use of a lead amalgam. The reduction of the 10 metal ions which are reduced to metal may be selectively abbreviated depending upon the variation in reduction potential of selective metal liquid amalgams.

The selective reduction of iron in the presence of titanium, as popularly provided by the use of the WALDEN silver reductor[4], could be similarly operative employing the bismuth liquid amalgam.

For most predictions of the reaction to be realized in any particular situation one needs only to be aware of the half cell redox potential of the elements for determination, and the reduction potential of the liquid amalgam selected. For the most rapid reaction kinetics it is well to observe that the reduction potential of the liquid amalgam should be 0.3 to 0.4 V lower than the reduction potential of the element to be determined.

LIQUID AMALGAM SEPARATORY REACTION FUNNEL DESIGN

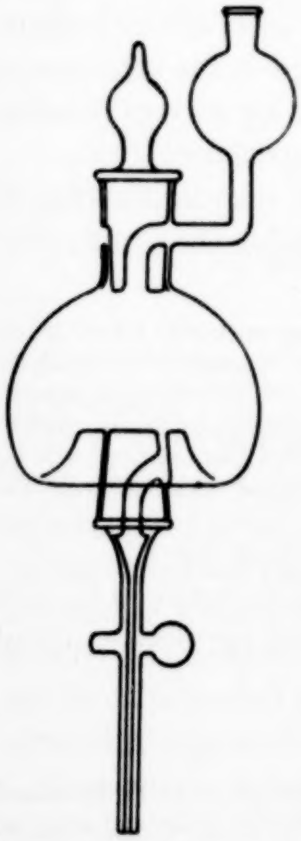

Fig. 1. Liquid amalgam separatory funnel.

A line drawing of the reaction and separatory funnel is shown in Fig. 1.

The body proper is of 450 ml capacity (made using a 500 ml round bottom flask). At the lower extremity, the efflux stopper is depressed within the body proper. A trough is thus formed to contain the liquid amalgam (volume approximately 50 ml). The amalgam capacity may be diminished to 25 ml or 15 ml as desired depending upon the extent to which the bottom stopper is depressed within the body proper.

The efflux stopper is provided with a side channel delivery tube in position for removal of the solution from the reaction chamber. This stopper is provided with a capillary discharge tube with lobes attached to facilitate adjustment.

The influx top stopper is designed with a side channel vent and an internal raceway tube. The vent channel matches a corresponding stopper bowl vent on one side. In the same position the tubular channel vent matches a tubular and 50 ml charging reservoir attached to one side of the ground glass dome stopper. With the bottom ground glass stopper closed and the dome stopper open, the device is ready to receive the selected contents.

First add sufficient liquid amalgam to fill the bottom trough just to the level of the top of the bottom stopper. Next add the solution to be reduced. Close the influx top stopper. Shake the contents of the apparatus vigorously to disperse the two liquid phases for 2 to 3 min or until the reaction of reduction is complete. Inverted funnel shaking is to be preferred.

A convenient support for the device is an iron ring tripod. It is expedient to wrap the iron ring with small bore rubber tubing to serve as a support cushion. By its use a beaker may be placed under the bottom delivery tube to receive the discharged, amalgam reduced, solution.

The device as described is suitable for the preparation of ferrous sulfate or vanadyl sulfate which are not reactive with atmospheric oxygen. If the intended preparation is,

References p. 509

for example, titanous sulfate solution the top ground glass stopper vent leading to the side channel should be a short length of tubular for use in attaching a rubber tubular leading to a reservoir of inert gas to displace the volume of solution withdrawn. For this manipulation the 50 ml side tube reservoir should be stoppered during withdrawals of the bowl contents. It is well to wire the bottom stopper securely in place by use of the exit tubular lugs and the bottom flange of the efflux stopcock. The selection of the most suitable liquid amalgam applied is a function of the reaction requirements in question.

THE PREPARATION OF STANDARD SOLUTIONS OF FERROUS SULFATE

The apparatus described may be used to advantage in the continuous preparation of standard solutions of ferrous sulfate. Since such solutions are not permanently stable in contact with air it is convenient to stock a large volume of 0.05 to 0.1 N ferric solution in 5 + 100 v/v of concentrated sulfuric acid and water. From this stock solution 400-425 ml of solution may be transferred to the amalgam reduction separatory funnel and reduced quantitatively upon time intervening service demands. By this technique the stock ferric sulfate solution requires but a single standardization. For this reaction a liquid zinc amalgam may be employed.

By use of a JONES reductor for this purpose the reaction of reduction is complete. One requirement in the use of the described reaction equipment and zinc amalgam reductor is that the shaking and reduction should be carried out in an inert gas. This is provided for if the charged separatory funnel has added to it a few ml of dilute sodium bicarbonate solution before shaking is applied to displace the air above the solution to be reduced. The air above the solution having thus been displaced by carbon dioxide the reaction of reduction is then complete after reduction by the liquid amalgam.

To demonstrate the need for this manipulation the reduction and standardization of a ferric sulfate solution using liquid zinc amalgam was carried out using the SMITH AND KURTZ[5] technique.

Without the use of the CO_2 atmosphere in contact with the solution being reduced, 25.00 ml of ferric sulfate solution after reduction, required (for reoxidation applying four consecutive titrations with Ce(IV) standard sulfate solution as oxidant and ferroine as indicator) the following volumes:

16.30, 16.35, 16.33, and 16.29 ml of oxidant—Av. 16.32 ml. The same volumes of ferric sulfate solution after reduction using the same zinc amalgam for reduction in an inert atmosphere of CO_2 and titrated employing the same procedure, the following volumes of the same oxidant were required:

16.47, 16.45, 16.50, 16.48, 16.42, 16.45, 16.51, 16.52 and 16.51 ml — Av. 16.48 ml.

No explanation has been found accounting for the divergent results between the use of solid and liquid amalgams as reductors. Similar results have been previously noted by SOMEYA[1] in studies employing liquid amalgam reductors.

SUMMARY

A new design of separatory funnel has been described which is used for the preparation of standard volumetric reductants and applies to the use of liquid metal amalgams. The new device may be employed in the reduction of individual samples of solutions for analysis but is to be employed primarily for the preparation and storage of small volumes of standard solutions. A description of operations illustrative in its usage have been given and its advantages described.

RÉSUMÉ

Un nouveau modèle d'entonnoir à séparation est décrit pouvant servir à la préparation de solutions étalon de réduction et utilisant des amalgames métalliques liquides. Cet entonnoir peut être employé pour la réduction de solutions à analyser, mais il est surtout recommandé pour la préparation et la conservation des solutions étalon. Les opérations effectuées ainsi que les avantages de ce procédé sont décrits.

ZUSAMMENFASSUNG

Ein neuer Scheidetrichter wird beschrieben, der zur Herstellung von reduzierenden volumetrischen Standardlösungen mit Hilfe von flüssigen Metallamalgamen benützt wird. Man kann ihn zur Reduktion einzelner zu analysierender Lösungsproben verwenden, doch soll er hauptsächlich zur Herstellung und Aufbewahrung kleiner Volumina von Standardlösungen dienen. Seine Anwendung wird durch die Beschreibung der Operationen verdeutlicht und seine Vorzüge werden dargelegt.

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THE APPLICATION OF THIOSALTS IN ANALYSIS

V. A NEW AND MORE COMPREHENSIVE SCHEME OF QUALITATIVE ANALYSIS

by

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In a series of papers[1-3] already published, a new scheme of qualitative analysis has been put forward including the common elements and some so-called rare elements which are of importance from industrial point of view. Detailed investigations in this laboratory have shown that the scheme which has already been put forward can provide a basis for a more comprehensive scheme including practically all the elements that a student is likely to find in qualitative analysis. The basic forming elements which have not been included so far can be fitted in the scheme making it more elaborate but unaltered as regards its main outline.

New elements have been included in the more comprehensive scheme proposed in this paper. As the properties of these elements, upon which their separations and detections are based, are already well known, it is proposed in this paper to give the details of the procedures which have to be adopted in the separation of the various elements into groups. Although the underlying principles of the procedures adopted in the more comprehensive scheme are the same, some modifications in the procedures have been rendered necessary owing to the inclusion of new elements.

Procedure I. Preparation of the solution and isolation of Os, Ru and Ge.

This may be divided into the following four steps.

(a) Isolation of osmium. The mixture is distilled with concentrated nitric acid (10 ml) in a quick-fit apparatus by heating the distilling flask on a hot asbestos plate. Osmium tetroxide being highly volatile distils over. The distillate is absorbed in $6N$ sodium hydroxide solution and distillation continued till about 3 ml of the acid is left in the distilling flask. A red colour in the sodium hydroxide solution is an indication of the presence of osmium in the mixture.

(b) Isolation of ruthenium. The residue left in (*a*) is further distilled with 10 percent nitric acid and 2-3 g of sodium bromate. Ruthenium tetroxide being volatile completely distils over, and is absorbed in $6N$ sodium hydroxide solution. The distillation is continued till about 3 ml of the acid is left in the distilling flask. A red colour in the sodium hydroxide solution shows the presence of ruthenium. Under these conditions germanium tetrabromide does not distil over. It has been found experimentally that even if the mixture contains considerable quantities of chlorides no germanium tetrachloride passes into the distillate under these conditions.

(c) Isolation of germanium. The residue left in (*b*) is further distilled with concentrated hydrochloric acid, when volatile germanium tetra-chloride distils over. This is absorbed in $6N$ sodium hydroxide solution.

The distillates are tested for osmium, ruthenium and germanium as given in Table I.

TABLE I

a) Distillate obtained with HNO_3	*b) Distillate obtained with 10 % HNO_3 and $NaBrO_3$*	*c) Distillate obtained with HNO_3 and HCl*
(1) To a portion add HCl to make it acid and then $Na_2S_2O_3$. Warm.	(1) To a portion add $2N$ Na_2S and CH_3COONH_4 in sufficient excess.	(1) To a portion add sufficient $2N$ Na_2S followed by a large excess of HCl.
A brown ppt. OsS_4 shows **Os**	A brown ppt. Ru_2S_3 shows **Ru**	A white flocculent ppt. GeS_2 shows **Ge**
(2) Acidify another portion with HCl. Add tannic acid and alcohol.	(2) Acidify another portion with HCl. Add NH_2OH. HCl.	Dissolve the ppt. in liquor ammonia and H_2O_2 by heating.
A dark blue coloration due to the formation of $OSCl_2$ shows **Os**	Disappearance of orange red colour in the solution due to reduction shows **Ru**	Add magnesia mixture. A white crystalline ppt. Mg_2GeO_4 shows **Ge**

(*d*). The residue from (*c*) is boiled with hydrochloric acid ($5N$ approximately), filtered and washed first with dilute acid and then several times with hot water. The filtrate contains the soluble portion of the mixture. The insoluble portion still left is treated separately for the detection of insoluble substances.

Procedure II

The acid solution containing all the basic radicals is treated with $4N$ sodium hydroxide to neutralize the large excess of the free acid (keeping it still acidic) and then with $2N$ sodium sulphide reagent in excess (adding 20 ml of the reagent in excess after the acid has been neutralized), 9-10 g of ammonium acetate followed by 2 g of sodium carbonate. It has been found that $2N$ sodium sulphide reagent brings about a more satisfactory separation but with this a larger quantity of ammonium acetate has to be added to ensure complete precipitation of metals like mercury, aluminium etc. The mixture is stirred thoroughly and filtered. The precipitate is washed with distilled water, the washings being added to the filtrate. The filtrate will contain the metals of arsenic group, Ni, Rh, In, Ga, magnesium and alkalis while the precipitate will contain the sulphides, hydroxides etc. of all other metals.

Procedure III

The filtrate containing the thiosalts is boiled with an excess of concentrated hydrochloric acid and 10-15 g of ammonium sulphate (added to completely precipitate rhenium as hepta-sulphide). The concentration of the acid in the resulting mixture is adjusted at a little above $6N$ in order to completely precipitate iridium, rhenium, rhodium, platinum and arsenic as sulphides.

The detailed analysis of the precipitate is given in Table II and that of the filtrate in Table III.

TABLE II

The precipitate may contain Ir_2S_3, PtS_2, Au_2S_3, TeS_2, As_2S_5, SeS_2, NiS, Rh_2S_3, Re_2S_7, MoS_3 and V_2S_5.
Dissolve the ppt. in conc. HCl and $KClO_3$. Evaporate to crystallization with KCl and filter. Wash the ppt. with a saturated solution of KCl

<table>
<tr>
<td colspan="2" rowspan="4">Ppt.
$K_2[IrCl_6]$ (brown)
$K_2[PtCl_6]$ (yellow)
Dissolve in HCl-HNO_3; evaporate to a small volume, add water and $NaHCO_3$ (solid) in excess and then bromine water or 10% $KBrO_3$ solution, boil and filter</td>
<td colspan="9">Fil. Au^{+3}, TeO_4^{-2}, AsO_4^{-3}, SeO_4^{-2}, Ni^{+2}, Rh^{+3}, ReO_4^-, MoO_4^{-2} and VO_4^{-3}.
Make it just alkaline with NaOH and add H_2O_2. Acidify with dil. HCl, boil and filter</td>
</tr>
<tr>
<td rowspan="8">Ppt.
Brown or black shows
Au</td>
<td colspan="8">Fil. TeO_4^{-2}, AsO_4^{-3}, SeO_4^{-2}, Ni^{+2}, Rh^{+3}, ReO_4^-, MoO_4^{-2} and VO_4^{-3}.
Concentrate to 10 ml, add 10 ml of conc. ammonia and then magnesia mixture. Filter</td>
</tr>
<tr>
<td colspan="2" rowspan="3">Ppt.
White
$Mg(NH_4)AsO_4 \cdot 6\ H_2O$ and $MgTeO_4$.
Dissolve in HCl, add Na_2SO_3, boil off SO_2 completely and filter</td>
<td colspan="6">Fil. SeO_4^{-2}, ammonia complexes of Ni and Rh, ReO_4^-, MoO_4^{-2} and VO_4^{-3}. Add enough 12N HCl to make the solution above 7N with respect to acid. Add Na_2SO_3, boil and filter</td>
</tr>
<tr>
<td rowspan="6">Ppt.
Red or black shows
Se</td>
<td colspan="5">Fil. Ni^{+2}, Rh^{+3}, ReO_4^-, MoO_4^{-2} and VO_4^{-3}.
Add dimethylglyoxime, make alkaline with ammonia and filter</td>
</tr>
<tr>
<td rowspan="5">Ppt.
Blue or black IrO_2 shows
Ir</td>
<td rowspan="5">Fil.
Add 12N HCl in excess, boil off bromine, evaporate nearly to dryness. Dissolve in water and add KI. Red coloration shows
Pt</td>
<td rowspan="5">Ppt.
Red shows
Ni</td>
<td colspan="4" rowspan="2">Fil. Rh^{+3}, ReO_4^-, MoO_4^{-2}, VO_4^{-3} and dimethylglyoxime. To remove dimethylglyoxime add 2-3 ml of conc. H_2SO_4 and evaporate to fumes. If charring takes place add nitric acid and heat again to fumes. Cool and dilute to 100 ml. Add titanous sulphate, boil for 2 min. and filter</td>
</tr>
<tr>
<td rowspan="4">Ppt.
Black shows
Te</td>
<td rowspan="4">Fil.
H_3AsO_3.
Add 2N Na_2S followed by HCl. A yellow ppt. As_2S_3 shows
As</td>
</tr>
<tr>
<td rowspan="3">Ppt.
Black shows
Rh</td>
<td colspan="3">Fil. ReO_4^-, MoO_4^{-2}, VO_4^{-3} and titanium sulphate. Add 2N Na_2S in excess followed by a large excess of 12N HCl and $(NH_4)_2SO_4$ to decompose the thiosalts. Boil and filter</td>
</tr>
<tr>
<td colspan="2">Ppt. Re_2S_7, MoS_3 and V_2S_5.
Treat with 2N Na_2S reagent in excess and filter</td>
<td rowspan="2">Fil.
Ti^{+4}.
Reject</td>
</tr>
<tr>
<td>Ppt.
Black
Re_2S_7.
Dissolve in aqua-regia and test for Re with nitron as usual</td>
<td>Fil. Thiosalts of Mo and V. Decompose with conc. HCl, boil and filter. Dissolve the sulphides ppt. in conc. HCl and $KClO_3$. Test as usual for Mo and V with NH_4CNS and H_2O_2 respectively</td>
</tr>
</table>

TABLE III

The solution may contain chlorides of V, (Ni), Sb, Sn, In, Ga, Mg and alkali metals. Boil off H_2S, add excess of H_2O_2 to oxidize vanadium to pervanadate and then $2N$ Na_2S in excess. Decompose the thiosalt with $1N$ hydrochloric acid and filter

<table>
<tr>
<td colspan="2">Ppt. V_2S_5, (NiS), Sb_2S_3 and SnS_2. Boil with $6N$ HCl and filter</td>
<td colspan="4">Fil. In^{+3}, Ga^{+3}, Mg^{+2} and alkali metal ions. Boil off H_2S. Add 2 g of NH_4Cl (solid), then NH_4OH until the solution is just alkaline. Filter</td>
</tr>
<tr>
<td rowspan="2">Ppt. V_2S_5 and (NiS). Dissolve in HNO_3 and test for V with H_2O_2 as usual</td>
<td rowspan="2">Fil. Sb^{+3}, Sn^{+4}.
Test as usual</td>
<td colspan="2">Ppt. $In(OH)_3$ and $Ga(OH)_3$. Dissolve in the minimum quantity of dil. HCl and treat with $2N$ Na_2S followed by an excess of CH_3COOH to make it $6N$ with respect to acid.
Boil and filter</td>
<td colspan="2">Fil. Mg^{+2} and alkali metals. Concentrate to a small volume, add NH_4OH and conc. $(NH_4)_2CO_3$ solution followed by an equal volume of alcohol. Filter</td>
</tr>
<tr>
<td>Ppt. Yellow In_2S_3. Wash the ppt., dissolve in HCl, add $K_4[Fe(CN)_6)]$. A white ppt. shows In</td>
<td>Fil. Gallium acetate.
Boil off H_2S.
Make it sufficiently acid with HCl and add $K_4[Fe(CN)_6]$. A white or bluish white ppt. shows Ga</td>
<td>Ppt. White $MgCO_3$ $(NH_4)_2CO_3 \cdot 6H_2O$. Confirm by cobalt nitrate test.
Pink mass shows Mg</td>
<td>Fil. Alkali metals.
(a) Test for Li, K, Rb and Cs as usual.
(b) If it is necessary to test the mixture for sodium by the wet method, a fresh portion of the solution containing all basic constituents may be treated with concentrated ammonium sulphide and filtered. From the filtrate the metals of arsenic and tin group are removed by decomposing the thiosalts and the solution tested for magnesium and alkalis including sodium</td>
</tr>
</table>

TABLE IV

This may contain HgS, PdS, PbS, Bi_2S_3, Tl_2S(TlI), Rh_2S_3, CuS, CdS, CoS and NiS. Boil the ppt. with HNO_3(1 : 2) for 4-5 minutes and filter

<table>
<tr>
<td rowspan="8">Ppt. Black or yellow. Confirm the presence of mercury as usual</td>
<td colspan="9">Fil. Pd^{+2} Pb^{+2}, Bi^{+3}, Tl^{+}, Rh^{+3}, Cu^{+2}, Cd^{+2}, Co^{+2} and Ni^{+2}. Dilute with 2 volumes of water.
(This will reduce the concentration of acid to 1-2<i>N</i>.) Add dimethylglyoxime in excess, digest on a steam bath for 45 min. and filter</td>
</tr>
<tr>
<td rowspan="7">Ppt. Yellow shows Pd</td>
<td colspan="8">Fil. Pb^{+2}, Bi^{+3}, Tl^{+}, Rh^{+3}, Cu^{+2}, Cd^{+2}, Co^{+2}, Ni^{+2} and dimethylglyoxime. Add 2-3 ml of conc. H_2SO_4 and evaporate to fumes.
If charring takes place add some conc. HNO_3 and heat again to fumes.
Allow to cool to the room temperature after removal of HNO_3, dilute to 100 ml and filter</td>
</tr>
<tr>
<td rowspan="6">Ppt. White $PbSO_4$ $(BiO)_2SO_4$. Dissolve in CH_3COONH_4 and confirm the presence of Pb by adding CH_3COOH and K_2CrO_4. A yellow ppt. shows Pb</td>
<td colspan="7">Fil. Bi^{+3}, Tl^{+}, Rh^{+3}, Cu^{+2}, Cd^{+2}, Co^{+2} and Ni^{+2}. Add H_2SO_3 to reduce thallic to thallous salt.
Add NH_4OH in excess and filter</td>
</tr>
<tr>
<td rowspan="5">Ppt. White $Bi(OH)_3$ shows Bi</td>
<td colspan="6">Fil. Tl^{+} and ammonia complexes of Rh, Cu, Cd, Co and Ni. Acidify the solution with HCl, boil off SO_2 and add bromine water to oxidize thallous to thallic salt.
Remove excess of bromine and add NH_4OH in excess. Filter</td>
</tr>
<tr>
<td rowspan="4">Ppt. Brown $Tl(OH)_3$ shows Tl</td>
<td colspan="5">Fil. Ammonia complexes of Rh, Cu, Cd, Co and Ni. Acidify with dil. H_2SO_4, reduce Rh and Cu with titanous sulphate and filter</td>
</tr>
<tr>
<td colspan="2">Ppt. Rh and Cu_2O. Treat with HNO_3 (1 : 2) and filter</td>
<td colspan="3">Fil. Cd^{+2}, Co^{+2}, Ni^{+2} and Ti^{+4}. Add 2<i>N</i> Na_2S in excess and filter (reject the filtrate). Treat the ppt. with 1<i>N</i> HCl for one min. and filter</td>
</tr>
<tr>
<td rowspan="2">Ppt. Black Dissolve in 10% HNO_3 and conc. H_2SO_4. Red solution of $Rh_2(SO_4)_3$ shows Rh</td>
<td rowspan="2">Fil. Copper nitrate. Test as usual for Cu</td>
<td colspan="2">Ppt. Sulphides of Cd, Co and Ni. Dissolve in the minimum quantity of HNO_3. Evaporate to dryness, take up the residue with very dilute hydrochloric acid, add 2<i>N</i> Na_2S acidified with dil. HCl and filter</td>
<td rowspan="2">Fil. Ti^{+4}. Reject</td>
</tr>
<tr>
<td>Ppt. Yellow CdS shows Cd</td>
<td>Fil. Co^{+2} and Ni^{+2}. Test as usual</td>
</tr>
</table>

TABLE V

The solution may contain CrO_4^{-2}, UO_5^{-2}, ZnO_2^{-2}, AlO_2^{-}, BeO_2^{-2}, GaO_3^{-3}, traces of indium or phosphate. (Test for phosphate. In case phosphate is present, indium will be completely absent, due to its precipitation as indium phosphate along with the metals of the iron group.) Acifidy with dilute nitric acid, add NH_4OH in excess and filter

<table>
<tr><td colspan="4">Ppt. $In(OH)_3$, $Al(OH)_3$, $Be(OH)_2$ and $(NH_4)_2U_2O_7$. Dissolve in the minimum quantity of dil. HCl. Treat with 2<i>N</i> Na_2S in excess followed by a large excess of acetic acid. (The concentration of the acid in the resulting solution should be about 6<i>N</i>.) Boil and filter</td><td colspan="3">Fil. May contain Cr, Zn and Ga. Add CH_3COOH and $BaCl_2$ in excess. Filter</td></tr>
<tr><td rowspan="3">Ppt. Yellow In_2S_3 shows In</td><td colspan="3">Fil. Acetates of U, Al and Be. Add NaOH in excess and filter</td><td rowspan="3">Ppt. Yellow $BaCrO_4$ shows Cr</td><td colspan="2">Fil. Zn^{+2} and Ga^{+3}, and Ba^{+2}. Add 2<i>N</i> Na_2S followed by sufficient excess of CH_3COOH and filter</td></tr>
<tr><td rowspan="2">Ppt. Yellow $Na_2U_2O_7$. Confirm the presence of uranium in the ppt. as usual</td><td colspan="2">Fil. $NaAlO_2$ and Na_2BeO_2. Add dil. HCl drop by drop till the ppt. formed just redissolves. Now add an excess of the oxine solution followed by 5 ml of saturated ammonium acetate and filter</td><td rowspan="2">Ppt. White ZnS. Confirm the presence of Zn as usual</td><td rowspan="2">Fil. Ga^{+3} and Ba^{+2}. Add sufficient excess of HCl and $K_4[Fe(CN)_6]$. A white or bluish white ppt. shows Ga</td></tr>
<tr><td>Ppt. Yellow $Al(C_9H_6ON)_3$ shows Al</td><td>Fil. Soluble complex of Be. Heat nearly to boiling and add a slight excess of ammonia solution. Brown or yellow ppt. shows Be</td></tr>
</table>

TABLE VI

The precipitate may contain oxalates of Ce, Th, Sc, Y, La and other rare-earths. Evaporate to dryness with conc. HNO_3 and $KClO_3$ to decompose the oxalates and oxidize cerous to ceric salt. Take up the residue with HNO_3 (1 : 1), add KIO_3 in excess and filter

<table>
<tr><td colspan="2">Ppt. $Th(IO_3)_4$ and $Ce(IO_3)_4$. Heat with H_2O_2 and (1 : 1) HNO_3 on a steam bath, add KIO_3 and filter. (Treatment with H_2O_2 and HNO_3 converts ceric to cerous salt[4])</td><td rowspan="2">Fil. Sc^{+3}, Y^{+3}, La^{+3} and rare-earths. The solution may be tested for the presence of the above mentioned elements by the well-known methods</td></tr>
<tr><td>Ppt. White $Th(IO_3)_4$ shows Th</td><td>Fil. Ce^{+3}. Add NH_4OH and H_2O_2. An orange ppt. shows Ce</td></tr>
</table>

TABLE VII

The precipitate may contain (Ta_2O_5), Nb_2O_5 and MnO_2. Heat the ppt. with an excess of oxalic acid and dil. H_2SO_4 to get a clear solution. Add 0.2 to 0.3 g of tannin followed by 0.5<i>N</i> NH_4OH drop by drop keeping the solution slightly acidic. Filter

<table>
<tr><td rowspan="2">Ppt. Pale to bright yellow shows Ta

In case the ppt. is orange owing to the coprecipitation of niobium repeat the whole process for the precipitation of tantalum. A yellow ppt. shows Ta</td><td colspan="2">Fil. Nb and Mn. Boil, treat with more tannin and 2-4 g of ammonium acetate. Filter</td></tr>
<tr><td>Ppt. Orange-red shows Nb</td><td>Fil. Add HNO_3 and $KClO_3$ to decompose tannic acid. Evaporate to dryness. Heat the residue with PbO_2 and conc. HNO_3. Violet coloration shows Mn</td></tr>
</table>

Procedure IV

Treat the precipitate obtained in Procedure II with cold 1*N* hydrochloric acid and potassium iodide for 1-2 minutes and filter immediately. This treatment dissolves all the compounds except the sulphides of the copper group. The detailed analysis of the precipitate is given in Table IV.

Procedure V

The filtrate from Procedure IV is treated with sodium hydroxide, sodium peroxide and sodium carbonate, boiled to decompose the excess of sodium peroxide and filtered while hot. The precipitate may contain the hydroxides, phosphates etc. of the metals belonging to the iron, rare-earth and alkaline earth groups and also lithium phosphate, in case lithium and phosphate both are present in the mixture. The filtrate will contain the metals of the aluminium group and is analysed according to Table V. Traces of phosphate may also pass into the filtrate but the presence of this acid does not interfere with the tests of the basic radicles.

Procedure VI

The precipitate obtained in Procedure V is dissolved in the minimum quantity of hydrochloric acid and the solution is diluted so that the concentration of the acid is about 0.5*N*, and then treated hot with an excess of a saturated solution of oxalic acid. This brings about a separation of Th, Sc, La and the rare earths from the remaining metals. Any precipitate of the oxalates formed is filtered off and analysed as in Table VI.

TABLE VIII

The precipitate may contain the basic acetates, phosphates and hydroxides of In, Ti, Fe and Zr. Dissolve the precipitate in the minimum quantity of 5*N* sulphuric acid, add a few pieces of granul-
boil for 5-10 minutes to completely precipitate In and filter

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ERRATUM

Anal. Chim. Acta, Vol. 16 (1957), page 515, in Table VIII:
Ti^{+4} should read Ti^{+3}
Fe^{+3} should read Fe^{+2}

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nt
O_3

Ppt. $BaCO_3$, $SrCO_3$, $CaCO_3$ and $MgCO_3(NH_4)_2CO_3$ Dissolve in the minimum quantity of dil. CH_3COOH and test for Ba, Sr, Ca and Mg as usual.	Test for lithium as usual

Procedure VII

The filtrate from Procedure VI which now contains the metals of the iron group, alkaline earths and lithium is evaporated to dryness with concentrated nitric acid to remove hydrochloric acid. The residue is boiled with concentrated nitric acid and potassium chlorate to decompose oxalic acid and to precipitate manganese, tantalum and niobium as oxides. The precipitate is filtered through asbestos and analysed as in Table VII.

Procedure VIII

The filtrate from Procedure VII containing the metals of the iron and alkaline earth groups and also lithium is tested for phosphate. In case phosphate is present, a small portion is tested for iron, the phosphate in the remaining solution is eliminated by the basic acetate method. If phosphate is absent ammonium hydroxide is added in excess and the precipitate filtered off. The precipitate containing the basic acetates, hydroxides and phosphates of In, Fe, Ti and Zr is analysed as in Table VIII and the filtrate containing alkaline earths and lithium according to Table IX.

References p. 516

SUMMARY

The scheme of qualitative analysis based on the formation and decomposition of thiosalts has been enlarged by including within it practically all the basic radicles which are likely to be met with in the analysis of ores and alloys, etc. Besides the rare elements already included in the original scheme rhodium, ruthenium, osmium, palladium, iridium, gallium, indium, rhenium, tantalum, niobium, germanium, scandium and the rare-earths and alkalis have been fitted into the more comprehensive scheme. An outline of procedures for the separation of metals into groups in the more comprehensive scheme of qualitative analysis is given.

RÉSUMÉ

La méthode d'analyse qualitative, basée sur la formation et la décomposition des thiosels, a été étendue à tous les radicaux basiques que l'on a des chances de rencontrer dans l'analyse des minerais, des alliages etc. En plus des éléments rares déjà compris dans la méthode originale, on a introduit encore les éléments suivants: rhodium, ruthénium, osmium, palladium, iridium, gallium, indium, rhénium, tantale, niobium, germanium, scandium, les terres rares et les métaux alcalins. Un aperçu est donné sur la séparation des métaux en groupes d'après cette méthode d'analyse qualitative.

ZUSAMMENFASSUNG

Das Schema der qualitativen Analyse, welches sich auf die Bildung und Zerstörung der Thiosalze gründet, wurde auf alle basischen Reste ausgedehnt, denen man bei der Analyse von Erzen, Legierungen, usw. begegnet. Neben den seltenen Elementen, welche das Schema bereits umfasste, wurden nun auch Rhodium, Ruthenium, Osmium, Palladium, Iridium, Gallium, Indium, Rhenium, Tantal, Niob, Germanium, Scandium und die seltenen Erden und Alkalien in das erweiterte Schema aufgenommen. Die Scheidung der Metalle in Gruppen nach dieser Methode wird umschrieben.

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[2] I. K. Taimni and G. B. S. Salaria, *Anal. Chim. Acta*, 13 (1955) 205.
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AN IMPROVED IODOMETRIC METHOD FOR THE SUCCESSIVE DETERMINATION OF COPPER AND ZINC

by

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S. Z. Haider and M. H. Khundkar[1] described a method for the successive iodometric determination of copper and zinc.

Copper was titrated by a modification of Bruhn's method and zinc was then titrated with thiosulphate after the addition of portions of ferricyanide solution.

The results were calculated on the basis of 1 ml N $Na_2S_2O_3$ equivalent to 0.0990 g Zn, a factor about 1% higher than theoretical.

Applying this procedure, we found however too low results for both copper and zinc (Table I).

TABLE I

Cu taken *m.equiv.*	*Zn taken* *m.equiv.*	*Cu found* %	*Diff.* %	*Zn found* %	*Diff.* %
1.037	1.146	82.8	—17.2	95.9	—4.1
1.037	1.146	81.7	—18.3	93.4	—6.6
1.037	1.146	78.3	—21.7	96.4	—3.6

According to H. W. FOOTE AND J. E. VANCE[2], the results found by the iodometric copper determination are too low, if the sulphocyanide is added at the start of the titration, as is prescribed by HAIDER AND KHUNDKAR. This is probably due to the reaction:

$$3I_2 + 6Cu^{+2} + 2CNS^- + 8H_2O \rightarrow 3Cu_2I_2 + 14H^+ + 2HCN + 2SO_4^{-2}$$

This reaction and the low results for copper can be avoided by adding the sulphocyanide at the end of the copper determination[2,3,4].

As a result of four determinations where the KCNS was added at the end of the copper titration, we found:

Cu: 99.9%, standard deviation of the mean, $s_m = 0.1\%$
Zn: 93.8%, ,, ,, ,, ,, ,, , $s_m = 1.7\%$.

In all determinations the precipitate underwent a dark-brown coloration during the titration of zinc, which made it very difficult to observe the end-point. This colour is due to the formation of $Cu_2[Fe(CN)_6]$ by the reaction:

$$2[Fe(CN)_6]^{-3} + Cu_2(CNS)_2 \rightarrow Cu_2[Fe(CN)_6] + [Fe(CN)_6]^{-4} + 2CNS^-$$

In order to prove that this reaction proceeds, KI and an excess of KCNS were added to a solution of $CuSO_4$ and the formed precipitate was filtered off, washed with water and suspended in a very dilute solution of $K_3[Fe(CN)_6]$ acidified with a few drops of H_3PO_4. The formation of $[Fe(CN)_6]^{-4}$ could be demonstrated by its reaction with Fe^{+3}.

Because the ferrocyanide ion formed by reduction of ferricyanide ion causes low results for zinc, the $Cu_2(CNS)_2$ must be removed from the solution before zinc is determined.

As the result of three determinations where the $Cu_2(CNS)_2$ was filtered off before the zinc titration, we found:

Zn: 98.3%, $s_m = 0.4\%$.

When zinc was titrated in this way we experienced much trouble from the fact that, when the solution was titrated to decolorization with thiosulphate, iodine was formed again after 0.5 — 2 minutes. This often recurred several times; CNS^- obviously shifts the equilibrium:

$$2[Fe(CN)_6]^{-3} + 3I^- + 2K^+ + 3Zn^{+2} \rightleftarrows K_2Zn_3\,[Fe(CN)_6]_2 + I_3^-$$

to the left, or it slows down the establishment of this equilibrium, possibly by forming complexes with Zn^{+2}.

It is therefore necessary to use a small quantity of KCNS in the copper determination so that there is no perceptible quantity of sulphocyanide ion left at the zinc titration.

References p. 519

It is inadmissible to omit the KCNS completely; as the mean of eight determinations without KCNS but with an excess of KI (6 g/g Cu) we found:

$$Cu: 99.3\%, s_m = 0.1\%.$$

About 1 g KCNS/g Cu proved however to be sufficient to give correct values for copper.

When copper was determined in a solution of copper and zinc sulphate, by means of 1 g KCNS/g Cu and 6 g KI/g Cu, the precipitate filtered off, and zinc determined in the filtrate, the values found for zinc were too low, *viz.* (mean of three determinations):

$$Zn: 98.5\%, s_m = 0.4\%.$$

When on the other hand copper was determined in this way in a copper sulphate solution, the precipitate filtered off and a solution of zinc sulphate added to the filtrate, the values found for zinc were nearly correct, *viz.* (mean of six determinations):

$$Zn: 99.6\%, s_m = 0.2\%.$$

Probably some zinc is adsorbed on the precipitate of $Cu_2(CNS)_2$. It appeared that this adsorption could be prevented by adding magnesium sulphate to the solution of copper and zinc before the KI is added. The quantity of $MgSO_4$ can be varied within wide limits.

In Table II the results of twenty determinations, performed according to this procedure, are given.

TABLE II

Cu taken m. equiv.	*Zn taken m. equiv.*	*0.8M $MgSO_4$ solution added ml*	*Cu found %*	*Diff. %*	*Zn found %*	*Diff. %*
1.127	0.986	2	99.8	—0.2	100.2	+0.2
1.127	0.986	2	99.6	—0.4	100.2	+0.2
1.127	0.986	2	100.0	0.0	99.8	—0.2
1.159	1.166	5	99.5	—0.5	100.0	0.0
1.159	1.166	5	99.8	—0.2	100.6	+0.6
1.159	1.166	5	100.1	+0.1	99.7	—0.3
1.159	1.166	5	100.2	+0.2	99.7	—0.3
1.159	1.166	5	100.2	+0.2	100.4	+0.4
1.159	1.166	5	100.6	+0.6	99.9	—0.1
1.159	0.986	15	99.6	—0.4	100.1	+0.1
1.159	0.986	15	99.5	—0.5	99.7	—0.3
2.818	0.986	2	100.1	+0.1	99.7	—0.3
2.818	0.986	2	99.9	—0.1	99.8	—0.2
2.818	0.986	2	100.1	+0.1	100.3	+0.3
2.818	0.986	5	99.8	—0.2	99.4	—0.6
2.818	0.986	5	99.8	—0.2	99.9	—0.1
2.818	0.986	5	99.8	—0.2	99.8	—0.2
2.818	0.986	15	100.1	+0.1	100.0	0.0
2.818	0.986	15	100.1	+0.1	100.2	+0.2
2.818	0.986	15	100.2	+0.2	100.6	+0.6

From Table II the mean of all values is found to be:

$$\text{Cu: } 99.9\%,\ s = 0.3\%,\ s_m = 0.1\%$$
$$\text{Zn: } 100.0\%,\ s = 0.3\%,\ s_m = 0.1\%$$

where s = standard deviation of a single determination, s_m = standard deviation of the mean.

We recommend the following method based on the above findings for the successive iodometric determination of copper and zinc:

Recommended method

A solution containing about 1 m.equiv. of zinc and 1-3 m.equiv. of copper is neutralized by adding NaOH solution till a turbidity just remains; this turbidity is removed by some drops of 25% phosphoric acid; 5 ml of a 0.8*M* $MgSO_4$ solution are added and after homogenization 6 g KI/g Cu are added. The iodine liberated is titrated with a 0.1*N* $Na_2S_2O_3$ solution until a slightly brownish colour remains. Now 2 ml of a 0.5% starch solution are added and the titration is continued till the blue colour starts to disappear. At this point 1 g KCNS/g Cu is added and the titration is completed.

The precipitate is filtered off and washed thoroughly with distilled water and subsequently with 10 ml of a 0.3*M* K_2SO_4 solution. To the filtrate is added a 0.2*M* $K_3[Fe(CN)_6]$ solution in 1 ml portions from a burette. Each time the liberated iodine is titrated to discoloration. The titration is complete when the blue colour does not reappear within 30 seconds.

1 ml *N* thiosulphate is equivalent to 0.0990 g Zn[3].

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SUMMARY

The method described by HAIDER AND KHUNDKAR for the succesive iodometric determination of copper and zinc gives results that are too low both for copper and for zinc. The errors may amount to —20% for copper and to —5% for zinc. The causes of these errors are traced and eliminated and an improved method for the succesive iodometric determination of copper and zinc is described.

RÉSUMÉ

La méthode décrite par HAIDER ET KHUNDKAR pour le dosage iodométrique successif du cuivre et du zinc donne des résultats trop faibles tant pour le cuivre que pour le zinc. Les erreurs peuvent aller jusqu'à —20% pour le cuivre et —5% pour le zinc. Les causes de ces erreurs sont recherchées et éliminées. Une méthode perfectionnée est décrite pour le dosage du cuivre et du zinc.

ZUSAMMENFASSUNG

Die Methode von HAIDER UND KHUNDKAR zur jodometrischen Bestimmung von Kupfer und Zink nacheinander ergibt für beide Metalle zu niedrige Resultate. Die Fehler können bis zu —20% für Kupfer und bis zu —5% für Zink betragen. Die Fehlerquellen wurden ermittelt und ausgeschaltet und eine verbesserte jodometrische Bestimmungsmethode beschrieben.

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THE FERRIC HYDROXAMATE COLOUR REACTION

PART I. THE DIRECT TITRATION OF WATER AND ACETIC ANHYDRIDE

by

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Hydroxamic acids give, in the presence of ferric salts, a highly coloured complex salt, the general formula of which may be written[1] $(RCO.NHO)_3Fe$. The ready formation of hydroxamic acids by the action of hydroxylamine on the appropriate anhydride led FEIGL, ANGER AND FREHDEN[2] to suggest that the development of such a colour might be conveniently employed to detect amounts of acid anhydrides as small as 5 γ. The reaction has here been used to provide an external indicator in the titration of water by acetic anhydride.

The reaction between acetic anhydride and water is slow but it is susceptible to general acid-base catalysis. Amongst the most powerful catalysts is perchloric acid and in the presence of a sufficient concentration of perchloric acid the direct titration of acetic anhydride against water becomes possible. Such titrations have been reported using the heat of reaction to follow its course[3]. In the present paper there is described a simple, rapid and accurate application of this titration to the estimation of water and alcohols using the ferric hydroxamate indicator.

EXPERIMENTAL

(a) *Apparatus*

Standard volumetric apparatus was used. Pipettes were rinsed in acetone after use and dried in a stream of warm air. Burettes and stock bottles were protected from atmospheric moisture though this precaution was subsequently found to be unnecessary.

(b) *Reagents*

Perchloric acid, acetic acid and acetic anhydride were of AnalaR standard. For part of the work a solution 0.1*N* of perchloric acid in acetic acid, supplied by B.D.H. for titrations in non-aqueous solution, was found to be satisfactory; subsequent supplies of this reagent were found to contain considerable amounts of free acetic anhydride and required treatment with the appropriate amount of water before being suitable for use. A solution of perchloric acid in anhydrous acetic acid may conveniently be made by treating aqueous perchloric acid (60%) with the calculated amount of acetic acid and acetic anhydride using the ferric hydroxamate colour reaction to control the final stages of the addition. Caution should be exercised during this dilution as the reaction between acetic anhydride and water is exothermic. The acetic anhydride may be diluted with acetic acid.

The indicator solution was prepared by dissolving hydrated ferric chloride (AnalaR) (1 g) in ethanol (100 ml.) to which hydrochloric acid (0.5 ml) had been added and then saturating with hydroxylamine hydrochloride (AnalaR). The solution was stored in a dark bottle; its sensitivity did not appear to deteriorate over a period of several weeks but in practice a fresh indicator solution was prepared every three days.

(c) *Concentration of perchloric acid*

A 0.1*N* solution of perchloric acid in acetic acid was diluted with moist acetic acid and the resulting solution titrated against acetic anhydride. The results (Table I), which have been corrected for the small titre due to water in the perchloric acid solution, indicated that at concentrations of perchloric acid greater than 0.04*N* the reaction proceeded rapidly enough to be used titrimetrically.

TABLE I

EFFECT OF NORMALITY OF PERCHLORIC ACID

Perchloric acid solution ml	*Acetic acid ml*	*Normality of perchloric acid*	*Titre*
25	0	0.10	0
20	5	0.08	0.124
15	10	0.06	0.256
10	15	0.04	0.372[a]
5	20	0.02	[b]

[a] Reaction is slow near the end-point.

[b] Reaction is too slow for the end-point to be observed.

(d) *Procedure*

An aliquot of the solution was diluted with a known volume of the solution of perchloric acid, and acetic anhydride was added slowly from the burette. Near the end-point, the approximate location of which had previously been determined, the anhydride was added dropwise. A drop of the solution was removed and added to one drop of the indicator solution and the mixture then diluted with five drops of water. This was repeated after each addition of the anhydride until, on subsequent examination, the end-point was detected as the change from a pale lemon colour to brown-pink; in the presence of a large excess of anhydride the indicator turns purple.

Blank titrations are necessary to allow for the presence of moisture in the perchloric acid solution and in any other diluent. The appropriate correction has been made in the results listed below.

RESULTS

Water

Mixtures containing known amounts of water in 0.1*N* solutions of perchloric acid in acetic acid were prepared and titrated against acetic anhydride. Table II shows that the method may be applied to the estimation of water over a wide range of concentrations. The upper limit is fixed partly by the necessity to preserve an adequate concentration of perchloric acid and partly by the nature of the reaction. It was found that the reaction is fast up to a water concentration of 20% but above this strength the reaction is slow. The reaction is exothermic and attempts to estimate the water content of 50% aqueous perchloric acid solutions led to violent explosions; no such vigorous reaction occurred at concentrations of 20% or less. The lower limit of applicability appears to be controlled solely by convenience and by the capacity of the apparatus.

TABLE II

ESTIMATION OF WATER

Strength of aqueous soln. %	*Weight of water taken* g	*Weight of water found* g
0.1	0.010	0.011
0.2	0.020	0.021
0.4	0.040	0.039
0.8	0.080	0.081
2	0.200	0.199
4	0.200	0.202
10	1.000	1.020
20	1.000	1.010
50	5.000	[a]

[a] No result obtained. See discussion in text.

The linearity of the titration over a wide range was shown by titrating varying amounts of aqueous acetic acid. The results (Fig. 1) fall on a straight line.

The method was found to be convenient for the estimation of the water content of a number of the familiar organic solvents. In particular, acetic acid, acetonitrile, ethyl acetate, acetone, benzene and carbon tetrachloride all readily gave accurate data. Since the Karl Fischer reagent may not be used directly to determine water in ketonic solvents or with reliability in acidic solvents, the superiority of the acetic anhydride titration in this field is apparent. Solvents, which under the reaction conditions exhibit a weakly basic character, notably the ethers (diethyl ether, 1,2-dimethoxyethane and tetrahydrofuran), cause the reaction to be slower than normal but do not prevent the determination of an end-point. The chloro-compounds ethylene dichloride and chloroform (but not carbon tetrachloride) give anomalous results in that the development of colour in the indicator is inhibited and spurious results are obtained.

Alcohols

The reaction between alcohols and acetic anhydride under these conditions is fast and the titration may be performed in a manner entirely analogous to that used for aqueous solutions. The full range of applicability was not explored, but there seems no reason to suppose it will not be as large as that found for aqueous solutions. Some typical results are shown in Table III. It is possible to estimate the amount of water present in alcohols by this method as the difference in the calculated and observed titres. The accuracy of such a procedure is low.

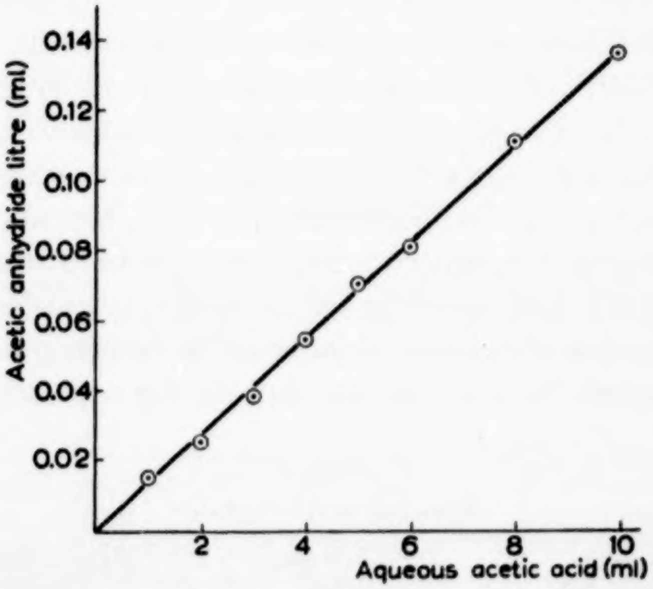

Fig. 1. The titration of aqueous acetic acid against acetic anhydride using the ferric hydroxamate indicator.

Amines

Under the conditions of the titration amines behave as strong bases and form salts with the perchloric acid. The acetylation reaction is thereby inhibited and the normal titrimetric procedure cannot be used. So slow was acetylation of amines under these circumstances that it was possible to estimate water in the presence on aniline with an accuracy apparently equivalent to that recorded for water alone.

References p. 523

TABLE III

ESTIMATION OF ALCOHOLS

Alcohol	*Weight of alcohol (96%)*[a] *g*	*Calculated titre ml*	*Observed titre ml*
Methanol	0.081	0.248	0.250
	0.163	0.498	0.50 0.490
	0.324	0.991	0.993 1.000
Ethanol	0.016	0.034	0.035
	0.032	0.068	0.072 0.072
	0.080	0.172	0.174
	0.163	0.350	0.350 0.352
	0.325	0.698	0.704

[a] Weight refers to total weight of sample, including 4% water. Calcd. titre is based on this mixture.

CONCLUSIONS

The ready accessibility of the reagents and the simplicity of the titration make this method particularly valuable. The convenience of the method is emphasised by the stability of the reagents which appear not to decay even over long periods; this may be contrasted with the behaviour of the solutions used in the Karl Fischer estimation. The method is applicable in those cases in which the use of the Karl Fischer titration is inadvisable, notably the estimation of water in ketones and in acids; it may also be used to estimate the water content of amines. The sensitivity of the method is good and an accuracy of ± 2% may be attained readily.

SUMMARY

The formation of the red colour of ferric acethydroxamate is used as an external indicator to follow the titration of water against acetic anhydride in the presence of perchloric acid. The method may be used for the estimation of alcohols. The technique proves to be rapid, convenient and accurate.

RÉSUMÉ

La formation de la coloration rouge de l'acéthydroxamate de fer(III) peut être utilisée comme indicateur externe lors du titrage de l'eau par l'anhydride acétique, en présence d'acide perchlorique. On peut employer cette méthode pour le dosage des alcools. La technique s'avère rapide, commode et exacte.

ZUSAMMENFASSUNG

Die Bildung der roten Farbe des Ferrisalzes der Acethydroxamsäure wird als äusserer Indikator benutzt um die Titration von Wasser mit Essigsäureanhydrid in Gegenwart von Perchlorsäure zu verfolgen. Die Methode kann zur Bestimmung von Alkoholen verwendet werden. Die Technik erweist sich als rasch, bequem und genau.

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ON MOHR'S METHOD FOR THE DETERMINATION OF CHLORIDES

by

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Mohr's method[1] for the determination of chlorides is one of the oldest titrimetric methods still in common use. Although it was once believed that certain adsorption indicators would supplant the original chromate indicator, because of their applicability at a lower pH and their greater sensitivity, the disturbing effect of electrolytes and the enhanced photodecomposition of the silver chloride precipitate are disadvantages which have prevented as extensive an application as was once expected, and Mohr's original method is still used.

The principle of this titration (formation of a coloured insoluble silver salt to mark the end-point) was first proposed by **Levol**[2] who used sodium phosphate or carbonate as indicator. **Mohr** examined sodium arsenate and potassium chromate but preferred the latter which gave a more distinct end-point; he did not specify the exact amount of indicator which he used. This aspect of the method and many others have been examined by a number of later investigators[3,4]. As late as 1939, **Berry and Driver**[5] pointed out a hitherto unsuspected source of error, namely the possibility of a change in pH beyond the limit of the permissible range when potassium chromate is added.

Despite the considerable amount of investigation to which this method has been subjected, there are still some conflicting statements made by various writers. For example, the methods which have been proposed for establishing the blank value differ widely; moreover many of the investigators subsequent to **Mohr** state that phosphate, arsenate and oxalate interfere and in one authoritative text-book, fluoride is said to interfere. As long ago as 1877 **Pellet**[6] claimed that phosphate, arsenite and arsenate had no influence on the titration because their silver salts are more soluble than silver chromate, but later investigators make no reference to his observations. **Mohr**'s method is said to be inapplicable to the titration of chlorides of metals which hydrolyse at the pH range within which the titration must be operated; hence it would be expected that the mere presence of such ions would have a baneful effect on the titration. Even on this subject there is disagreement and contradiction. We have been unable to find any reference to the effect of aluminium ion amongst the extensive literature on this subject, although several text-books state that it interferes; some writers ascribe this interference to the formation of an insoluble basic chloride. **Treadwell and Hall**[7] state that aluminium does not interfere, provided that sufficient sodium acetate is added to bring the pH within the permissible range.

Another text-book[8] states that zinc chloride cannot be titrated owing to its hydrolysis but, according to **Kolthoff**[9], zinc acetate may be used to remove sulphide, which presumably would leave an excess of zinc ions in the solution. Iron is said by some writers to interfere because it forms an insoluble chromate; whether the interference is caused by this, or by precipitation of ferric hydroxide, or by losses owing to the precipitation of a basic chloride is of little practical importance, because in every case the colour change at the end-point would be masked. However, it might be possible to overcome this interference by the addition of a suitable masking agent, provided that it formed a colourless complex ion with the ferric ion.

In view of these conflicting statements we have considered it desirable to examine the various conditions in turn.

(1) *The determination of the blank value*

Blanks were determined by four different methods:

(a) With water alone,
(b) With a suspension of calcium carbonate,
(c) With a suspension of freshly precipitated, well-washed silver chloride,
(d) By the back-titration method.

After some practice under these different conditions, no significant differences in titre could be observed. In all cases, the blank value was equivalent to 0.05 ml of 0.1*N* silver nitrate or to 0.12 ml of 0.05*N* silver nitrate, in a volume of 75 ml. This value would undoubtedly vary with different operators. The amount of indicator had no noticeable effect over the range 0.5-1.0 ml of a 5 per cent (0.52*N*) solution. The washed silver chloride had very different properties from that produced during an actual titration and it was impossible to simulate exactly the true conditions. The washed silver chloride, which was always affected by light, settled rapidly to the bottom of the titration vessel and would not remain in suspension. The end-point conditions were readily simulated when a suspension of calcium carbonate was used and this method is recommended.

(2) *The use of sodium phosphate and arsenate as indicators*

In view of PELLET's observations it was considered desirable to re-check the indicator properties of sodium phosphate and arsenate. Solutions of the same normality as that of the potassium chromate indicator (0.52*N*) were used and blank values were determined using calcium carbonate in suspension. The results are included in Table I.

TABLE I

Indicator added	*Vol. of indicator used*	*Titre found ml $AgNO_3$*	*Blank ml $AgNO_3$*	*Titre after deducting blank*	*Theor. titre*	*Error %*
0.52*N* Na_2HPO_4	1	25.30	0.20	25.10	25.00	0.4
	5	25.30	0.20	25.10	25.00	0.4
0.52*N* Na_3AsO_4	1	25.20	0.15	25.05	25.00	0.2
	5	25.20	0.15	25.05	25.00	0.2

The blanks were higher than those obtained with potassium chromate as indicator. Even when allowance was made for them, the results were slightly high. The colour change, especially with sodium phosphate, was much more difficult to see than that given by potassium chromate.

(3) *The effect of the indicator on the pH of the solution*

The effective pH range of the method was checked and was found to be 6.5-10.3. Solutions of varying pH were treated with neutralised and un-neutralised indicator and the pH was re-determined (Tables II and III). As will be seen, the addition of 1 ml of un-neutralised indicator to a solution having a pH of 5.6-9.2 resulted in a final pH of 8.1-8.9, whereas the neutralised indicator when added to a solution of pH 5.5-10.0 brought the final pH range to 6.9-7.1. It is well-known that when ammonium salts are present the pH should not exceed 7.2, otherwise the end-point comes too late; hence there appears to be a definite source of error when the un-neutralised indicator is used. BERRY AND DRIVER's recommendation that neutralised indicator be used is thus supported. Because of the buffer action of the indicator it will automatically maintain the optimum pH range, even though that of the original solution lies between 5.5-10.0.

TABLE II

Adjusted pH →	5.6	6.10	6.80	7.95	8.40	8.65	8.90	9.20
After add. 0.5 ml K_2CrO_4	8.0	8.0	8.1	8.3	8.4	8.5	8.7	9.0
After add. 1.0 ml K_2CrO_4	8.1	8.1	8.2	8.3	8.5	8.5	8.6	8.9
After add. 2.0 ml K_2CrO_4	8.2	8.2	8.3	8.4	8.5	8.5	8.6	8.8

The pH of the $0.52N$ K_2CrO_4 was 8.5

TABLE III

Adjusted pH →	5.5	7.0	8.0	10.0
After addition of 0.5 ml neutral indicator	6.8	6.9	7.0	7.2
After addition of 1.0 ml neutral indicator	6.9	6.9	7.0	7.1
After addition of 2.0 ml neutral indicator	6.9	6.9	7.0	7.1

BERRY AND DRIVER suggested that instead of neutralising the chromate indicator with nitric acid a mixture of potassium chromate and potassium dichromate might be used. They did not specify the proportions to be used to give a neutral solution. We found that one ml of a solution containing 4.2 g of potassium chromate and 0.7 g of potassium dichromate per 100 ml gave the best results, but the ratio of chromate to dichromate could vary from 4.2 : 0.6 to 4.2 : 0.8 with little difference in the pH attained (Table IV).

TABLE IV

Indicator ratio g : g	*Amount added ml*	*pH of 25 ml of 0.1N NaCl (initial pH = 5.6) diluted to*		
		25 ml	*50 ml*	*100 ml*
4.2 : 0.6	1	7.1	7.0	7.0
4.2 : 0.7	1	7.0	7.0	7.0
4.2 : 0.8	1	7.0	6.9	6.9

The intermediate solution contains 13.7 mg of chromium per ml whereas the usual 5 per cent chromate indicator contains 13.4 mg. The mixed indicator solution, which is more convenient to prepare, can be recommended in place of the indicator neutralised with nitric acid.

(4) *The effect of phosphate, arsenate, fluoride and oxalate*

When phosphate or arsenate was added to the chloride solution, slightly high titres were obtained. As would be expected on theoretical grounds, the titres increased with increasing amounts, but the errors were by no means pronounced (see Table V); they could possibly be tolerated in certain types of analysis. The effect of these ions is certainly less marked than is generally supposed. Fluoride had no effect in the concentrations tried. Moderate amounts of oxalate caused a slight positive error; larger amounts increased this error and the end-point became more difficult to detect. The effect of oxalate was decreased by the addition of calcium nitrate, but the results were still slightly high unless calcium carbonate was also added to maintain the pH at the correct level. Better end-points were obtained when a slight excess of 2*N* nitric acid was added to the solution containing chloride, oxalate and calcium carbonate. In this case, the results were only 0.1 per cent high when 200 mg of potassium oxalate were present.

TABLE V

Salt added	*Amount added* g	*Increase in titre* ml
Na_2HPO_4	0.122	0.05
	0.245	0.06
	0.490	0.07
Na_3AsO_4	0.180	0.04
	0.720	0.05
KF	0.151	none
	0.604	none
$K_2C_2O_4$	0.086	0.10
	0.216	0.25
	0.432	no definite end-point

(5) *The effect of iron, zinc and aluminium*

No attempt was made to discover the actual composition of the precipitate which caused the interference of iron (*cf.* p. 524); for whatever the composition, the end-point would be masked by the colour. The addition of fluoride masked the interference to a certain extent provided that enough potassium fluoride was added to precipitate potassium fluoferrate. After the addition of sodium bicarbonate or calcium carbonate to adjust the pH, a coloured precipitate did not appear, but the final results were about 0.7-0.9 per cent high and the end-points were not very satisfactory. EDTA was also tested for masking the interference of iron; the red colour of the ferric complex masked the end-point of the MOHR titration and there was also some indication that EDTA alone had an adverse effect on the end-point. This was not unexpected.

There was no evidence of any interference from zinc (up to 130 mg — the highest amount tested) when a solution of zinc nitrate was added to sodium chloride. The mixture was titrated with and without the addition of calcium carbonate; the results were the same.

Because of the conflicting statements in the literature regarding the effect of aluminium, some titrations were done without any attempt being made to prevent its possible interference, apart from adding calcium carbonate to adjust the pH. When 20 ml of 0.1*N* sodium chloride were titrated, 5 ml of 0.1*M* aluminium nitrate caused no interference, but 25 ml gave a positive error of 0.7 to 1 per cent. This error could not be avoided by the use of fluoride to complex the aluminium, nor by the use of sodium bicarbonate to give a higher final pH. Since text-books refer to the fact that aluminium chloride cannot be titrated, rather than to the effect of aluminium on the titration, a solution of aluminium chloride was titrated by the MOHR method (after adding calcium carbonate) and by the VOLHARD method. The MOHR titration showed a positive error of 0.5-0.7 per cent in a final titre of 30 ml of 0.1*N* silver nitrate. This is the result which would have been expected from the results of the previous experiments with aluminium nitrate. It seems probable that this slight interference is caused by an electrolyte effect which increases the solubility of silver chromate.

EXPERIMENTAL

(1) The standard silver and chloride solutions were prepared by weighing the appropriate amounts of the pure salts; they were checked against each other in the presence of dichlorofluorescein as indicator.

The blank values were determined:

(a) By adding the silver nitrate solution to 75 ml of water containing 1 ml of 0.52*N* potassium chromate indicator until the first perceptible change of colour occurred.

(b) and (c) were done exactly as in (a) but 0.26 g of calcium carbonate and 0.35 g of well-washed silver chloride were added to the respective solutions.

(d) The chloride solution was titrated to the first perceptible change of colour. It was then titrated back with 0.01*N* sodium chloride solution to the original tint.

The blank values were finally checked by titrating 25 ml amounts of 0.1*N* sodium chloride solution with standard silver nitrate in the presence of potassium chromate indicator. The difference between the titre obtained and the titre when dichlorofluorescein was used as indicator (the blank value is negligible for dichlorofluorescein) checked the values obtained by the more direct methods.

(2) To examine the behaviour of arsenate and phosphate as indicators, varying amounts of 0.52*N* sodium phosphate or arsenate were added to 25 ml of 0.1*N* sodium chloride solution and the mixture was diluted to 50 ml with water. This solution was then titrated in the usual way until a colour change was observed.

(3) The effect of the indicator on the pH of the solution was examined by adjusting the pH to the desired value with 0.01*N* alkali or acid. A Marconi pH meter with calomel and glass electrodes was used for the pH measurement. An amount of neutralised, un-neutralised or mixed indicator was then added and the pH was redetermined. The neutralised indicator was adjusted to pH 7 with 0.01*N* nitric acid using the pH meter.

(4) The effect of the various anions was examined by adding an appropriate amount to 25 ml of sodium chloride solution, diluting to 50 ml, adding 1 ml of indicator and titrating with 0.1*N* silver nitrate.

For the removal of oxalate as calcium oxalate, calcium carbonate was added to the solution followed by enough 2*N* nitric acid to give a slight excess of calcium ion in solution over that required for the precipitation. The mixture was then shaken thoroughly for some moments before titration.

CONCLUSIONS

The most convenient method for determining the blank value is the use of a suspension of calcium carbonate. For general purposes about 0.25 g of calcium carbonate is suitable but if the amount of chloride to be titrated is much smaller or larger than say 0.1 g, smaller or larger amounts of calcium carbonate should be used. The calcium carbonate is added to a volume of water approximately equal to that likely to be obtained in an actual titration, indicator is added and the titration is done with a more dilute solution of silver nitrate than is used in the actual determination, until a colour change is observed.

If arsenate or phosphate is present in moderate amounts, its effect is not serious and could possibly be tolerated for many purposes, or allowed for by an appropriate correction. Fluoride ion has no effect on the titration. Oxalate interferes at all concentrations but can be removed by precipitation as calcium oxalate if nitric acid is added to the solution containing calcium carbonate.

Contrary to statements made in various text-books, zinc does not interfere in the

MOHR titration. Small amounts of aluminium do not interfere and moderate amounts cause only a slight positive error. The interference of iron can be overcome to some extent by precipitation of the iron as potassium ferrifluoride; however, the results and the end-point of the final titration are then not very satisfactory. EDTA does not appear to be of value for masking the effect of interfering cations.

The final pH of the solution after the addition of indicator should lie between 6.5 and 10.3; if ammonium salts are present the maximum pH should be 7.2. One ml of neutralised 5 per cent potassium chromate indicator can be used. An indicator which is more convenient and which gives the same effect as neutralised indicator can be prepared from potassium chromate and potassium dichromate in the ratio 4.2 : 0.7 by weight per 100 ml of water; 1 ml of this solution is used per titration. These neutral indicators will maintain the pH of the solution at about 7 because of their buffering effect.

SUMMARY

MOHR's method for the determination of chloride has been re-examined because of a number of conflicting statements which still appear in the text-books. Methods for the determination of the blank value have been compared. Evidence was found in support of BERRY AND DRIVER's claim that the indicator should be neutralised; a much better control of the final pH value of the solution is thus obtained. The effect of phosphate and arsenate was found to be less serious than is generally supposed; fluoride had no effect at all. Oxalate interferes seriously but the interference can be overcome by precipitation as calcium oxalate. Iron also interferes but can be partially masked with fluoride. Contrary to the general opinion aluminium causes only slightly high results and zinc is without effect. Attempts to mask cations which normally interfere by the use of EDTA were unsuccessful.

RÉSUMÉ

La méthode de MOHR, pour le dosage des chlorures, a été examinée à nouveau pour étudier certains points au sujet desquels des auteurs sont en contradiction. Les méthodes pour l'essai à blanc ont été comparées. D'accord avec les travaux de BERRY ET DRIVER, il a été établi que l'indicateur devrait être neutralisé; un bien meilleur contrôle du pH final de la solution est ainsi obtenu. L'influence du phosphate et de l'arséniate est moins nuisible qu'on le suppose généralement. L'anion fluorhydrique n'a aucun effet. Les oxalates gênent considérablement mais il est possible de les éliminer au préalable sous forme d'oxalate de calcium. Le fer gêne également mais il peut être partiellement masqué par un fluorure. Contrairement à ce qu'on croit généralement, en présence de l'aluminium, les résultats obtenus ne sont que légèrement trop forts; le zinc est sans effet. Les essais effectués pour masquer certains cations au moyen de EDTA n'ont pas été concluants.

ZUSAMMENFASSUNG

Die MOHR'sche Methode zur Bestimmung der Chloride wurde aufs Neue untersucht um einige strittige Punkte aufzuklären. Die Methoden zur Bestimmung des Blanko-Wertes wurden verglichen. In Übereinstimmung mit dem Befunde von BERRY UND DRIVER wurde ermittelt, dass der Indikator neutralisiert werden sollte; man erhält dann eine viel bessere Regelung des End-pH-Wertes der Lösung. Der Einfluss von Phosphat und Arseniat ist weniger schädlich als allgemein angenommen wird; Fluorid is wirkungslos. Oxalat stört stark; diese Störung kann aber durch Fällung als Calciumoxalat aufgehoben werden. Auch Eisen stört, kann aber teilweise mit Fluorid getarnt werden. Im Gegensatz zu der allgemein herrschenden Meinung verursacht Aluminium nur um ein weniges erhöhte Resultate und ist Zink wirkungslos. Versuche zur Tarnung störender Kationen mit EDTA waren ergebnislos.

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MESURE DU THORIUM À L'ÉCHELLE DU MILLIMICROGRAMME

par

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INTRODUCTION

L'étude de la répartition naturelle de l'uranium et du thorium à l'état de traces offre un grand intérêt en géochimie et en géophysique. Avec les méthodes actuellement connues, les limites de détection sont beaucoup plus basses pour l'uranium que pour le thorium: il est possible de mesurer des quantités d'uranium de l'ordre de 10^{-10} g par la méthode fluorimétrique, alors qu'il est difficile de mesurer des quantités de thorium inférieures à 10^{-6} g. La méthode la plus sensible actuellement connue semble être la dilution isotopique[1].

Nous décrivons ici une méthode radioactive permettant la mesure du thorium à l'échelle de 10^{-9} g. Elle est basée sur l'observation dans les émulsions photographiques nucléaires des „étoiles" d'α formées à partir du radiothorium. Nous avons déjà appliqué cette méthode à la mesure du thorium dans l'océan[2] et les sédiments océaniques[3].

PRINCIPE DE LA MÉTHODE

Les méthodes radioactives de mesure du thorium sont basées sur la mesure de l'activité α, non pas du Th-232, mais d'un de ses descendants. La raison principale en est l'impossibilité de séparer chimiquement le Th-232 de ses isotopes α-actifs: l'ionium, le radiothorium et le radioactinium.

Les méthodes radioactives ont une sensibilité essentiellement limitée par la faible activité spécifique du thorium: un microgramme de Th-232, ou n'importe lequel de ses descendants en équilibre avec cette quantité, subit $4 \cdot 10^{-3}$ désintégration par seconde, soit 14 par heure. Le „background" des meilleurs compteurs d'α est de l'ordre de quelques impulsions par heure.

Pour accroître la sensibilité, il faut introduire une discrimination basée, par exemple, sur le spectre d'énergie des α ou encore, sur la distribution des intervalles de temps séparant deux désintégrations α successives[4]. On pourrait ainsi accroître facilement d'un facteur 10 la limite de détection, mais la mesure devrait porter sur des temps d'une dizaine de jours pour avoir une précision statistique de 10%.

L'émulsion photographique nucléaire[5] représente le détecteur de particules α le plus sensible connu à ce jour. Grâce à ses propriétés de localisation et d'intégration dans le temps, ce détecteur possède la caractéristique unique d'enregistrer les désintégrations successives d'un atome radioactif individuel pendant des périodes de plusieurs semaines ou de plusieurs mois, sous la forme bien connue d'étoiles de trajectoires partant d'un même point[6]. La probabilité de formation d'étoiles d'une multiplicité donnée est très différente pour les divers nuclides radioactifs et offre un moyen aisé de discrimination[7].

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Bibliographie p. 540

La proportion des divers types d'étoiles en fonction du temps d'exposition est donnée à la Fig. 1 pour le cas de la famille du Th en équilibre.

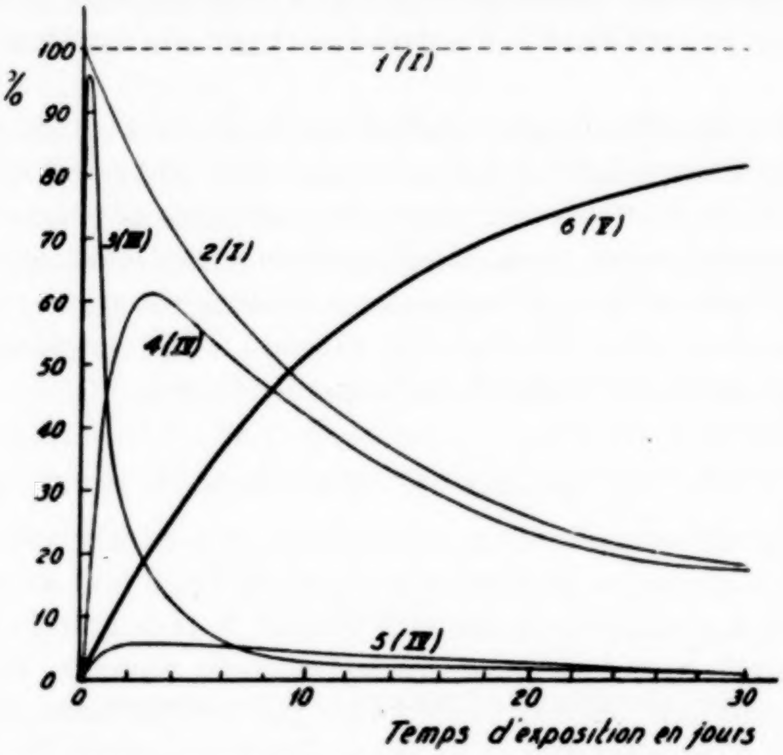

Fig. 1. Nombre d'événements pour 100 désintégrations du Th en équilibre avec ses descendants, en fonction du temps d'exposition.
1 = α simples du Th
2 = α simples du RdTh
3 = Étoiles à 3 branches: ThX→Tn→ThA→ThB
4 = Étoiles à 4 branches: ThX→Tn→ThA→[ThB→]Th(C+C')→ThD
5 = Étoiles à 4 branches: RdTh→ThX→Tn→ThA→ThB
6 = Étoiles à 5 branches: RdTh→ThX→Tn→ThA→[ThB→] Th(C+C')→ThD.

Pour un temps d'exposition de l'ordre du mois, le calcul conduit aux conclusions suivantes:

1. Les nuclides U-238, U-235, U-234, Th-230 (Io), Th-232 et Po-210 ne produisent que des traces simples.

2. Dans les trois familles en équilibre, la probabilité de formation d'étoiles à 2 branches ou à plus de 5 branches est toujours nulle.

3. Aucun des nuclides appartenant à la famille de l'U-238 ne forme d'étoiles à plus de 4 branches.

4. Les seuls nuclides donnant lieu à des étoiles à 5 branches sont le Th-228 (RdTh) et le Th-227 (RdAc).

La méthode décrite ici est basée sur la formation des étoiles à 5 branches à partir du RdTh. Elle présente les avantages suivants:

a) L'émulsion nucléaire est un détecteur stable et sensible en permanence. En prenant les précautions nécessaires pour réduire l'effacement de l'image latente, on peut prolonger la mesure sur des périodes de plusieurs mois et compenser ainsi la faible activité spécifique du Th.

Bibliographie p. 540

b) Le ,,background'' des émulsions nucléaires est de 10 à 50 fois plus faible pour les étoiles à 5 branches que pour les traces simples[8] (Tableau V).

c) L'observation microscopique des étoiles est beaucoup plus aisée que celle des traces simples.

d) Si on néglige l'interférence du RdAc qui sera discutée plus loin, les étoiles à 5 branches sont entièrement spécifiques du RdTh et permettent de mesurer ce nuclide en présence d'un excès considérable d'autres émetteurs α et notamment de son isotope, l'Io.

Pour appliquer cette méthode, il est indispensable que le thorium soit introduit dans l'émulsion à l'état de dispersion atomique, c'est-à-dire en vraie solution. Si cette condition n'est pas remplie, les étoiles d'α pourraient être dues, non pas aux désintégrations successives d'un même atome, mais à des groupements d'atomes radioactifs.

Les principales difficultés expérimentales à résoudre sont: la mise en solution de l'échantillon et la séparation chimique du thorium, l'introduction du thorium dans l'émulsion photographique et enfin, la diffusion du thoron.

SÉPARATION DU THORIUM

Quoique la méthode soit spécifique du RdTh, il est généralement nécessaire d'effectuer une séparation chimique de tous les isotopes du Th; il faut les concentrer dans un volume minimum de solution de façon à obtenir la plus grande activité spécifique possible. On dispose, pour la séparation de traces de thorium, de méthodes basées sur les échangeurs d'ions[9] ou sur l'extraction par des solvants organiques tels que l'hexone[1], l'oxyde de mésityle[10,11] et la thénoyltrifluoroacétone[12]. L'expérience nous a montré qu'il est indispensable de vérifier le rendement des opérations chimiques à l'aide d'un radiotraceur. Le radioisotope naturel le mieux adapté à cet usage est l'UX_1 (Th-234, émetteur β de 24.1 jours de période) qu'il est facile de préparer à l'état très pur, sans trace de RdTh[13].

Nous ne discuterons pas ici le problème purement chimique de la séparation du thorium, problème très variable suivant la nature et la quantité d'échantillon disponible. On trouvera dans les articles cités plus haut une description des procédés chimiques utilisés dans le cas de l'eau de mer[2], des argiles pélagiques[3] et des roches silicatées[1].

INTRODUCTION DU THORIUM DANS L'ÉMULSION

L'émulsion photographique étant très sensible aux agents chimiques, on doit contrôler strictement la nature des solutions qu'on y introduit. Un facteur essentiel est le pH des solutions qui doit être voisin de la neutralité. Pour maintenir le thorium en solution à un pH voisin de 7, nous l'avons complexé par les ions citriques. Des expériences antérieures nous ont montré qu'en dehors d'une légère contraction de la gélatine, l'imprégnation de l'émulsion par une solution 0.1 M de citrate de sodium ne produit aucun effet nuisible sur le processus photographique.

Nous avons montré aussi[14] que le procédé le plus efficace pour introduire quantitativement la solution radioactive dans l'émulsion consiste à déposer et à évaporer des gouttes de volume connu entre deux couches d'émulsion et à compter toutes les particules α émises dans le volume occupé par la goutte. Cette technique assure une géométrie de 4π et supprime les difficultés classiques inhérentes aux comptages absolus d'activités α.

DIFFUSION DU THORON

On sait que la distribution des divers types d'étoiles prévue par la théorie n'est pas confirmée par l'observation, à cause de la diffusion des radioéléments dans l'émulsion.

L'étoile à 5 branches du RdTh est le plus souvent scindée en une étoile à 2 branches et une étoile à 3 branches à cause de la diffusion du thoron.

On peut observer aussi d'autres modes de dissociation: une étoile à 4 branches et une trace simple (diffusion du ThX), une étoile à 3 branches et deux traces simples (diffusion du ThX et du thoron).

En général, les déplacements dus à ces diffusions sont suffisamment petits pour que l'on puisse aisément reconnaître la multiplicité initiale de l'étoile dissociée. Le thoron, cependant, peut migrer à une distance telle que l'étoile à 3 branches ne soit plus associée à l'étoile à 2 branches, ou même ne se forme pas à cause de la diffusion du thoron hors de l'émulsion. Dans ce cas, l'étoile à 2 branches reste le seul témoin de la désintégration d'un atome de radiothorium.

Dans un article récent[15], nous avons montré qu'il est possible d'arrêter toute diffusion en exposant les émulsions à basse température (—35° pour la famille du thorium).

Le Tableau I montre la fréquence relative de ces divers types de dissociation à 3 températures.

TABLEAU I

FRÉQUENCE RELATIVE OBSERVÉE DES DIVERS TYPES DE DISSOCIATION DES ÉTOILES À 3, 4 ET 5 BRANCHES DANS LA FAMILLE DU THORIUM

Température d'exposition		*—35°C*	*0°C*	*18°C*
E_3	E_3	100	100	59
	$E_2 + a$	0	0	41
E_4	E_4	93	48	54
	$E_3 + a$	7	44	43
	$E_2 + E_2$	0	8	3
E_5	E_5	92.7	52.5	54
	$E_3 + E_2$	0.3	39.5	30
	$E_3 + 2a$	0	2	2.5
	$E_4 + a$	6	4	8.5
	E_2	1	2	5

E_n = étoile d'a de multiplicité n
a = trace d'a simple

Nous démontrerons ici qu'il est suffisant, pour le dosage du radiothorium, d'exposer les émulsions à 0° environ, *à condition de comprendre dans les désintégrations du RdTh, non seulement les étoiles à 5 branches vraies, mais aussi les étoiles provenant d'une façon visible de la dissociation d'une étoile à 5 branches et les étoiles à 2 branches.*

VÉRIFICATION DE LA MÉTHODE

La méthode a été vérifiée sur des solutions étalon de teneur connue en thorium et en radiothorium.

Bibliographie p. 540

A. Préparation des étalons

Deux étalons radioactifs de thorium en solution ont été préparés à partir de nitrate de thorium d'âge connu; leurs caractéristiques sont données au Tableau II.

La concentration en thorium a été mesurée par gravimétrie de ThO_2.

La pureté chimique du thorium a été vérifiée par comparaison spectrophotométrique avec une solution étalon de thorium spectroscopiquement pur (Matthey et Johnson) en utilisant la coloration formée avec le ,,Toron''.

Le rapport d'équilibre (rapport des activités RdTh/Th) a été calculé par les équations de Bateman avec les valeurs des périodes données au Tableau III.

TABLEAU II

CARACTÉRISTIQUES DES SOLUTIONS ÉTALON

	Th I	*Th II*
Nature:	$Th(NO_3)_4$ dans HCl 0.1*M*	$Th(NO_3)_4$ dans HCl 0.1*M*
Origine:	Institut Océanographique, Göteborg	Institut du Radium, Paris
Equilibre Th-RdTh:	$\varphi > 99.5\%$ (sel vieux de plus de 50 ans)	$\varphi = 86.7\%$ (MsTh séparé en 1931)
Concentration en Th:	(4.25 ± 0.01) mg Th/ml	(3.76 ± 0.04) mg Th/ml
Pureté du Th:	> 99%	> 99%

TABLEAU III

PÉRIODES DES MEMBRES DE LA FAMILLE DU THORIUM

Th	$= 1.39 \cdot 10^{10}$ an	Tn	= 54.5 sec
$MsTh_1$	= 6.7 an	ThA	= 0.158 sec
RdTh	= 1.9 an	ThB	= 10.6 h
ThX	= 3.64 j	ThC	= 60.5 min

B. Dépôt et calibration des gouttes

Les étalons Th I et Th II ont été dilués 250 fois dans une solution à pH 7.3, d'acide citrique et de citrate de sodium 0.2*M* en ions citriques. Des gouttes de $2 \cdot 10^{-3}$ ml de ces solutions ont été déposées avec une microseringue Agla sur des plaques Ilford C_2 de 100 μ. Elles ont été recouvertes, après séchage, d'une goutte d'émulsion C_2 ,,in gel form'', d'environ 0.05 ml.

Un certain nombre de gouttes témoins ont été préparées sur les mêmes plaques pour l'estimation du ,,background'' de l'émulsion.

Le volume exact des gouttes délivrées par la microseringue a été calibré par pesée. On a tenu compte de l'évaporation en extrapolant à zéro la courbe d'évolution du poids au cours du temps. La moyenne d'un grand nombre d'essais donne, pour le volume d'une goutte:

$$(1.95 \pm 0.03) \cdot 10^{-3} \text{ ml}$$

L'erreur représente la déviation standard sur la moyenne; la déviation standard sur une goutte est de $\pm 0.07 \cdot 10^{-3}$ ml.

C. Exposition, développement et observation microscopique

Après séchage, les émulsions ont été conservées dans des boîtes hermétiques contenant du silicagel, pendant des temps variant de 10 à 27 jours. Les expositions ont été réalisées à 0° et à —35°C. Les plaques exposées à —35° étaient préparées sur support d'acétate de cellulose[16].

Toutes les plaques ont été développées par la méthode à deux températures[17] avec le révélateur suivant[18]:

Pour 1000 ml d'eau:

Amidol	4.5 g
Acide borique	35 g
Sulfite de sodium anhydre	18 g
Bromure de potassium	0.8 g
Stade d'imprégnation à 4°	60 min
Stade chaud à sec à 20°	60 min
Bain d'arrêt, acide acétique 1%	10 min
Fixage à 18° dans le thiosulfate à 30%	4 h environ
Lavage	10 h

L'observation microscopique a été effectuée à un grossissement de 500 fois. Tout le volume correspondant à la double couche d'émulsion a été exploré et toutes les trajectoires d'α ont été notées et classées suivant leur présentation en trace simple ou en étoile.

Résultats obtenus

La quantité de thorium contenue dans une goutte est donnée, en microgrammes, par:

$$\boxed{C_{\mathrm{Th}} = \frac{E_5}{\nu S\,(t)\,.\,\varphi}}$$

où $\nu S\,(t)$ = nombre d'étoiles à 5 branches produites pendant le temps t par la quantité de RdTh en équilibre avec 1 microgramme de Th-232
t = temps d'exposition
E_5 = nombre d'étoiles à 5 branches formées dans la goutte
φ = nombre de désintégrations du RdTh pour une désintégration du Th.

$S(t)$ a été calculé d'après l'équation donnée par SENFTLE *et al.*[7]. Les valeurs de φ pour les deux solutions sont données au Tableau II.

D'après la quantité de thorium contenue par goutte, on a calculé pour chaque temps d'exposition le nombre théorique, non seulement d'étoiles à 5 branches, mais aussi des autres types d'événements, toujours d'après les formules de SENFTLE *et al.*

Les nombres calculés sont comparés aux résultats des observations microscopiques dans les Tableaux V, VI et VII. Ces résultats sont corrigés pour le ,,background" des émulsions. Dans les nombres d'étoiles observées sont comprises les étoiles dissociées. Les E_5 comprennent en outre les étoiles à 2 branches.

Le Tableau IV donne les valeurs du ,,background" observé dans les essais à blanc pour les divers types d'événements. Ces valeurs sont comparables à celles données par DEUTSCH ET DODD[8].

TABLEAU IV

,,BACKGROUND" DE L'ÉMULSION ILFORD C_2 (PURIFIÉE)
(le volume moyen de l'émulsion sèche correspondant à une goutte est de $3\cdot 10^{-3}$ ml)

type d'événement	a	E_2	E_3	E_4	E_5
Nombre moyen par jour et par goutte	0.1	0.01	0.02	0.01	0.002

α = trace d'α simple
E_n = étoile de multiplicité n

Discussion des résultats

1) Les concentrations en thorium calculées à partir du nombre d'étoiles à 5 branches correspondent, dans les limites des fluctuations statistiques, aux concentrations réelles; c'est la démonstration de la validité de la méthode. Sur les 30 gouttes comptées, une seule a donné un résultat aberrant et a été exclue dans le calcul des moyennes données au Tableau VII.

2) A la condition de comprendre dans les E_5 les étoiles à 5 branches dissociées et les étoiles à 2 branches, il n'y a pas de différence systématique entre les résultats des plaques exposées à 0° et à —35°. Il n'est donc pas nécessaire de maintenir les plaques à une température inférieure à 0°.

Bibliographie p. 540

TABLEAU V

Solution Th I ($\varphi = 1$). Nombre d'événements par goutte de $1.95 \cdot 10^{-3}$ ml, Th par goutte $= 33.1 \cdot 10^{-9}$ g

Température d'exposition	*Temps d'exposition en jours*	α		E_3		E_4		E_5		C_{Th} (10^{-9}g)[a]
		calc.	*obs.*	*calc.*	*obs.*	*calc.*	*obs.*	*calc.*	*obs.*	
—35°C	3.8	85	86	4.5	11	34	24	10.2	10	32.0
,,	9.9	177	211	1.4	5	62	64	56.4	82	b
0	,,	,,	200	,,	6	,,	56	58	61	34.7
—35	13.9	229	244	0.6	7	69	63	99	100	33.3
,,	,,	,,	255	,,	2	,,	54	,,	92	30.6
0	,,	,,	289	,,	6	,,	75	,,	87	28.9
—35	16.9	266	278	0.4	4	71	67	132	139	34.7
0	,,	,,	299	,,	5	,,	69	,,	138	34.4
—35	19	289	296	0.25	3	73	64	166	146	31.1
,,	26.9	385	399	0.06	1	74	75	247	258	34.6
0	,,	,,	424	,,	12	,,	93	,,	267	35.8
Sommes:		2540	2770	10	62	728	704	1279	1298	

[a] Quantité de Th en 10^{-9} g par goutte, calculée d'après E_5

[b] Exclu de la moyenne

Chaque ligne se rapporte à une goutte.

TABLEAU VI

Solution Th II ($\varphi = 86.7\%$). Nombre d'événements par goutte de $1.95 \cdot 10^{-3}$ ml, Th par goutte $= 29.3 \cdot 10^{-9}$ g

Température d'exposition	*Temps d'exposition en jours*	α		E_3		E_4		E_5		C_{Th} (10^{-9}g)
		calc.	*obs.*	*calc.*	*obs.*	*calc.*	*obs.*	*calc.*	*obs.*	
—35°C	9	139	122	1.3	5	45	43	38	35	27
,,	,,	,,	123	,,	5	,,	53	,,	40	30.8
0	,,	,,	126	,,	0	,,	40	,,	40	30.8
—35	13	185	209	0.6	5	51	62	69	68	28.9
,,	,,	,,	199	,,	8	,,	47	,,	53	22.5
,,	,,	,,	196	,,	5	,,	53	,,	64	27.2
,,	,,	,,	184	,,	3	,,	47	,,	68	28.9
0	,,	,,	182	,,	1	,,	40	,,	74	31.5
,,	,,	,,	178	,,	10	,,	42	,,	73	31.1
—35	16	218	223	0.3	1	53	52	94	86	26.8
,,	,,	,,	191	,,	5	,,	59	,,	94	29.3
0	,,	,,	219	,,	5	,,	51	,,	112	34.9
,,	,,	,,	231	,,	0	,,	53	,,	90	28.0
—35	18	240	243	,,	3	54	70	112	117	30.8
,,	26	324	300	0.05	10	55	63	182	179	28.9
,,	,,	,,	293	,,	6	,,	60	,,	161	26.0
,,	,,	,,	327	,,	5	,,	70	,,	164	26.4
0	,,	,,	322	,,	4	,,	61	,,	189	30.5
,,	,,	,,	272	,,	4	,,	48	,,	187	30.1
Sommes:		4259	4140	9	85	982	1014	1926	1894	

3) Bien que seuls les résultats de la colonne E_5 interviennent dans le calcul de la concentration en Th, on notera la bonne concordance entre les résultats observés et calculés pour tous les autres types d'étoiles. Dans l'étalon Th I, le rapport α/E_5 observé est supérieur de 7% au rapport théorique. Cet excès de traces simples peut être dû à l'ionium, le thorium proviendrait dans ce cas d'un minerai contenant 2% d'U par rapport au Th.

Bibliographie p. 540

TABLEAU VII

CONCENTRATION EN THORIUM CALCULÉE D'APRÈS LES ÉTOILES À 5 BRANCHES. MOYENNE DE TOUTES LES GOUTTES OBSERVÉES

	E_5		C_{Th} (10^{-9}g)		$\alpha/\Sigma E_5$	
	calc.	*obs.*	*calc.*	*obs.*	*calc.*	*obs.*
Th I	1313 ± 36[a]	1298	33.1	33.6 ± 0.6[b]	1.99 ± 0.07[a]	2.13
Th II	1926 ± 43[a]	1894	29.3	29.1 ± 0.4[b]	2.21 ± 0.06[a]	2.19

[a] dispersion théorique due aux fluctuations statistiques sur le nombre de désintégrations

[b] dispersion expérimentale sur la moyenne des gouttes

Les étoiles à 4 branches proviennent en grande majorité du ThX (Ra-224), la concordance des nombres calculés et observés des E_4 démontre que le radium est resté en solution stable pendant tout le processus bien que sa concentration soit de l'ordre de 10^{-17} g/ml.

Il y a un excès d'étoiles à 3 branches, même à —35°, qui peut être attribué à la diffusion du thoron pendant le séchage et le développement des émulsions.

4) La dispersion des résultats expérimentaux correspond bien à la dispersion sur le volume moyen des gouttes. Elle est du même ordre que la dispersion due aux fluctuations statistiques du nombre de désintégrations.

INTERFÉRENCE DU RADIOACTINIUM

Le RdAc (Th-227) est le seul nuclide qui donne lieu également à des étoiles à 5 branches. Il est chimiquement inséparable du RdTh. Son effet est généralement négligeable, grâce à la faible contribution de la famille de U-235 par rapport à celle du Th-232, dans les échantillons naturels. Lorsque les deux familles sont en équilibre dans l'échantillon, la contribution du RdAc aux étoiles à 5 branches dépend du rapport chimique Th/U, et, à un degré moindre, du temps d'exposition de l'émulsion photographique. Si l'actinium a été éliminé dans la fraction finale contenant les isotopes du thorium, la contribution du RdAc décroît avec le temps τ écoulé depuis la séparation de l'Ac jusqu'au dépôt de la solution, temps pendant lequel le RdAc ($T = 18.9$ jours) a décru.

Nous donnons, dans la Fig. 2, la proportion des étoiles à 5 branches dues au RdAc, en fonction de τ et du rapport Th/U dans l'échantillon. Pour le rapport Th/U = 3, qui est le rapport moyen dans la croûte terrestre, l'interférence du RdAc est toujours inférieure à 2%. Pour les valeurs du rapport Th/U comprises entre $3 \cdot 10^{-2}$ et 1, il est nécessaire de séparer l'Ac et de laisser décroître le RdAc pendant un à deux mois avant de faire la mesure, si on veut maintenir la contribution du RdAc inférieure à 10%. Lorsque le rapport Th/U est inférieur à 10^{-2}, le nombre d'étoiles à 5 branches dues au RdAc est du même ordre ou supérieur à celui des étoiles du RdTh. La méthode devient inapplicable si on n'introduit pas un critère permettant de discriminer les étoiles du RdTh de celles du RdAc.

En principe, on dispose des trois critères suivants:

1) L'évolution du nombre d'étoiles en fonction du temps d'exposition,
2) L'évolution du nombre d'étoiles en fonction du temps τ,
3) La longueur des branches d'étoiles (présence du ThC′).

Bibliographie p. 540

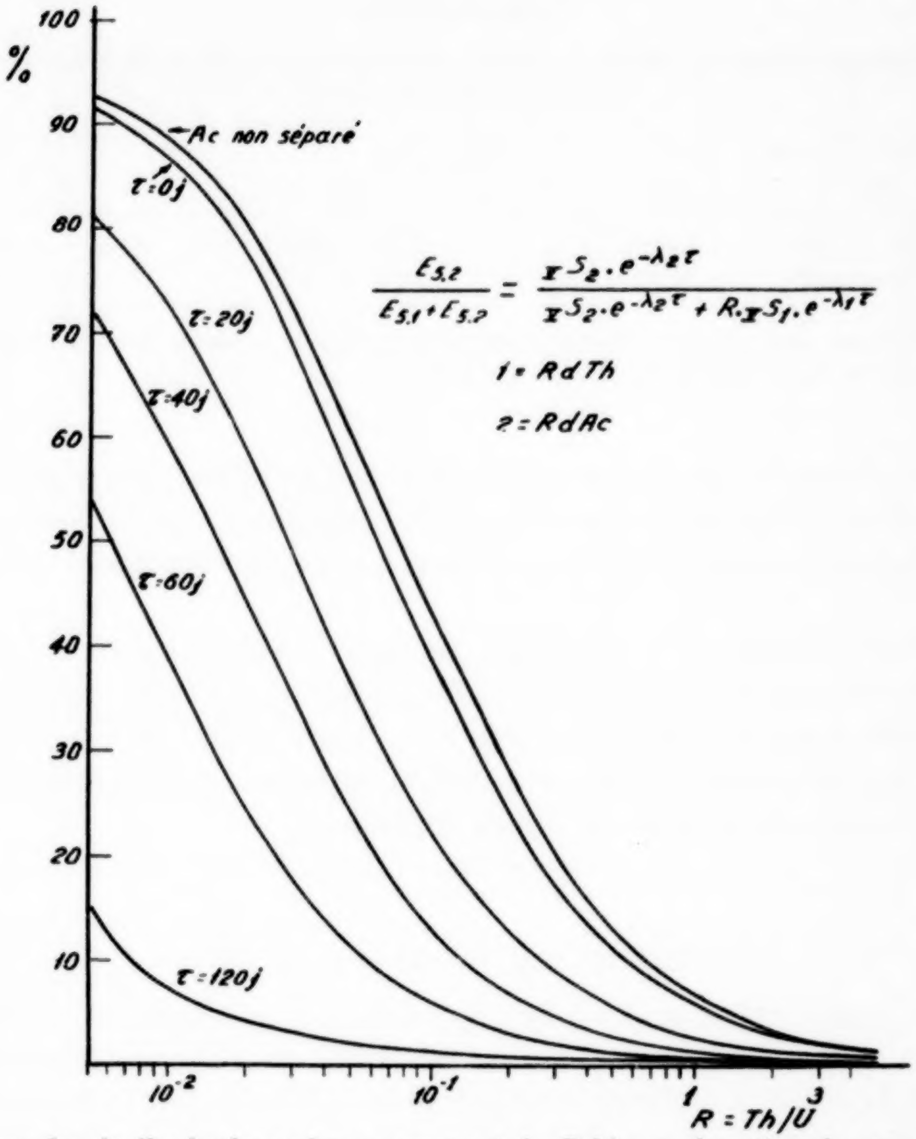

Fig. 2. Proportion des étoiles à 5 branches provenant du RdAc en fonction du rapport Th/U, pour différentes valeurs du temps τ écoulé depuis la séparation de l'Ac.

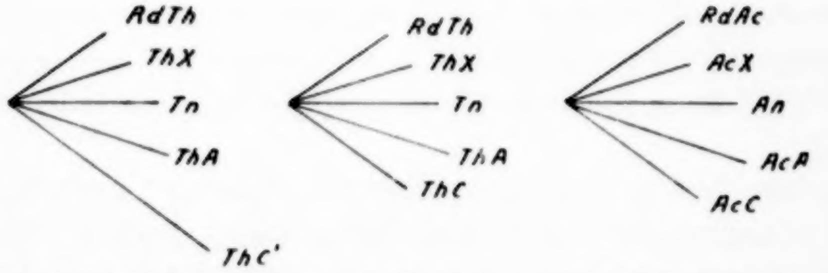

Fig. 3. Longueurs relatives des branches des trois types possibles d'étoiles à 5 branches.

Le troisième critère est le plus utile. La Fig. 3 représente les longueurs relatives des branches des 3 types possibles d'étoiles à 5 branches. Les étoiles contenant la trajectoire de l'α du ThC' se distinguent facilement des 2 autres, grâce à la longueur de cette trajectoire. L'estimation des longueurs des trajectoires très inclinées est facilitée en réduisant la contraction de l'émulsion[19].

Si on désigne par E_5' le nombre d'étoiles à 5 branches contenant l'α du ThC', le nombre total d'étoiles à 5 branches dues au RdTh est, avec la plus récente valeur du rapport d'embranchement du ThC[20]:

$$E_5 = 1.58 \cdot E_5'$$

En se basant uniquement sur les étoiles à branches longues, on peut encore mesurer le RdTh avec une bonne approximation pour des rapports Th/U de l'ordre de $5 \cdot 10^{-4}$.

TABLEAU VIII

LONGUEURS DES BRANCHES DES DIFFÉRENTS TYPES D'ÉTOILES À 5 BRANCHES

RdTh	23 μ	RdAc	27.2 μ
ThX	24.7 ,,	AcX	24.8 ,,
Tn	28.7 ,,	An	32.4 ,,
ThA	32.1 ,,	AcA	36.4 ,,
ThC	27.6 ,,	AcC	31.0 ,,
ThC′	47.5 ,,		

CONCLUSIONS

La méthode de mesure du RdTh décrite ici est valable pour le thorium lorsque le rapport d'équilibre Th-RdTh est connu. Rappelons que l'équilibre radioactif dans la famille du Th est établi à 99.5% en 50 ans.

Interférences. Il n'y a aucune interférence des éléments non radioactifs. Parmi les nuclides radioactifs, le seul qui pourrait interférer est le radioactinium, mais sa contribution est négligeable tant que le rapport Th/U dans l'échantillon est supérieur à 10^{-2}.

Sensibilité. La limite de détection est de 10^{-9} g de Th. Pendant une exposition de 100 jours, qu'il est facile de réaliser sans fading appréciable, 10^{-9} g de Th produit 30 étoiles à 5 branches. Si on suppose le Th réparti dans 10 gouttes de $2 \cdot 10^{-3}$ ml, le „background" moyen correspondant sera de 2 étoiles.

Précision. Les erreurs expérimentales sont de l'ordre de 3%. L'erreur sur les périodes du Th-232 et de ses descendants est négligeable[21]. Pour les très basses concentrations (10^{-9} à 10^{-7} g), la précision des résultats est limitée par les fluctuations statistiques sur le nombre d'étoiles. Avec une exposition de 100 jours, on pourrait déterminer $3 \cdot 10^{-9}$ g de Th avec une dispersion de ± 10%. Pour les concentrations plus élevées, il n'y a pas d'intérêt à compter plus d'un millier d'étoiles. Il est utile de répartir les mesures sur 10 à 20 gouttes pour diminuer l'incertitude sur le volume moyen des gouttes.

Inconvénients. Les principaux inconvénients sont: la longueur des temps d'exposition, la durée des observations microscopiques et les facteurs subjectifs qui y sont liés, la nécessité de concentrer le Th dans un volume final très petit, l'appel à une technique photographique d'application délicate. Pour ces raisons, la méthode décrite ici se prête mal aux mesures en grande série. Elle présente néanmoins l'avantage d'être la seule capable, à l'heure actuelle, de mesurer des quantités de thorium de l'ordre de 10^{-9} g.

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Bibliographie p. 540

RÉSUMÉ

Le Th en solution est mesuré par les étoiles de particules α formées, dans les émulsions photographiques nucléaires, à partir du RdTh. La technique décrite permet de détecter le RdTh en équilibre avec 10^{-9} g de Th, contenu dans un volume de quelques centièmes de ml, en présence de tous les autres nuclides stables ou radioactifs. La précision est principalement limitée par les fluctuations statistiques du nombre de désintégrations; les erreurs expérimentales sont de l'ordre de ± 3%.

La méthode a été vérifiée sur des solutions étalon. Les techniques expérimentales, la diffusion du thoron et l'interférence du RdAc sont discutées d'une façon détaillée.

SUMMARY

Thorium in solution is measured by the tracks of α-particles, formed from RdTh, in nuclear photographic emulsions. Using the method described, it is possible to detect RdTh in equilibrium with 10^{-9} g Th, contained in a volume of several hundredths of a millilitre, in the presence of all the other stable or radioactive nuclides. The accuracy is chiefly limited by the statistical fluctuations of the number of disintegrations; the experimental errors are in the order of ± 3%.

The method has been checked on standard solutions. The experimental techniques, diffusion of thoron, and interference of RdAc, are discussed in detail.

ZUSAMMENFASSUNG

Das Thorium in Lösung wird durch die „Sterne" der aus RdTh in den photographischen Emulsionen gebildeten α-Teilchen gemessen. Die beschriebene Arbeitstechnik gestattet, das RdTh im Gleichgewicht mit 10^{-9} g Th in einem Volumen von einigen Hundertstel ml in Gegenwart aller anderen stabilen und radioaktiven Nukliden nachzuweisen. Die Genauigkeit wird hauptsächlich durch die statistischen Schwankungen der Anzahl Zerfälle beschränkt; die experimentellen Fehler sind von der Ordnung von ± 3%.

Die Methode wurde an Hand von Standardlösungen geprüft. Arbeitstechnik, Diffusion des Thorons und Störung durch RdAc werden ausführlich besprochen.

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THE Fe(III)-EDTA-H_2O_2 COMPLEX AND ITS ANALYTICAL USE*

by

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If an excess of hydrogen peroxide is added to a solution containing the Fe(III) complex of ethylenediaminetetraacetic acid (EDTA), and if the solution is then made ammoniacal, an intensive red-violet colour appears. This phenomenon has previously been described by CHENG AND LOTT[1], by SCHNEIDER AND JANKO[2] and by RINGBOM[3].

The intensity of the colour depends on the excess of hydrogen peroxide and on the pH of the solution. The EDTA concentration has to be at least equivalent to the amount of iron. According to various considerations and calculations, it is likely that the iron-EDTA complex and hydrogen peroxide react in the molar ratio 1 : 1.

The complexity constant can be determined if the intensity of the red-violet colour of the complex formed is measured. In Table I some values are given allowing the calculation of an apparent constant K' defined by

$$\frac{[\text{Fe-EDTA-H}_2\text{O}_2]}{[\text{Fe-EDTA}]\,[\text{H}_2\text{O}_2]} = K'$$

The red-violet compound formed is designed by Fe-EDTA-H_2O_2 and the iron-EDTA compound by Fe-EDTA. The exact formulas of these complexes will be discussed later on.

TABLE I

DETERMINATION OF THE APPARENT STABILITY CONSTANT

pH	*[H_2O_2]* $\times 10^2$	*Absorbance*	*[Fe-EDTA-H_2O_2]* $\times 10^4$	*[Fe-EDTA]* $\times 10^4$	*log K'*
9.45	3.57	0.259	4.78	4.87	1.44
,,	6.98	0.345	6.36	3.29	1.44
,,	10.49	0.385	7.10	2.55	1.42
,,	14.00	0.433	7.99	1.66	1.54
10.65	0.652	0.345	6.36	3.29	2.47
,,	0.999	0.399	7.36	2.29	2.51
,,	1.353	0.417	7.70	1.95	2.47

The H_2O_2 values are corrected, *i.e.* [Fe-EDTA-H_2O_2] is subtracted from the total concentration of hydrogen peroxide added. The measurements were made at 22°.

A Beckman spectrophotometer, model B, and light of 520 mμ was used. At this wavelength only the violet complex absorbs appreciable amounts of light.

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* Part of this paper was presented at the IUPAC Congress in Lisbon in September 1956.

The absorbance index of the peroxide compound was determined using a large excess of hydrogen peroxide. The obtained value demands a small correction, since the reaction is usually not sufficiently complete. The correction can be made on the basis of the determined value of K'.

At a given pH value K' shows a good constancy, but with increasing pH also K' increases. In Table II the results of some series of measurements are given.

TABLE II

THE STABILITY CONSTANT AT VARIOUS PH VALUES

pH	$\log K' = \log \frac{[Fe\text{-}EDTA\text{-}H_2O_2]}{[Fe\text{-}EDTA]\,[H_2O_2]}$	$\log K = \log \frac{[Fe\text{-}EDTA\text{-}H_2O_2]}{[Fe\text{-}EDTA]\,[O_2H^-]}$
9.45	1.44	3.74
10.20	2.10	3.66
10.65	2.47	3.60
10.95	2.68	3.54
11.45	3.10	3.57
		average: 3.62

If the $[H_2O_2]$ values in K' are replaced by the values of the perhydroxyl ion concentration $[O_2H^-]$ calculated from the acidic dissociation constant of hydrogen peroxide $= 10^{-11.75}$, a new constant K is obtained which is given in the last column of Table II. The relationship between K' and K is

$$K = K'\left\{1 + 10^{11.75}\,[H^+]\right\}$$

It is seen that a good constancy of K is obtained. This fact proves that the reaction occurs between O_2H^- ions and the Fe-EDTA complex and that hydrogen ions are neither consumed nor liberated at the reaction.

SCHWARZENBACH AND HELLER[4] have investigated the hydroxyl complexes of the iron-EDTA complex and have shown that in an alkaline solution two complexes with one and with two hydroxyl groups exist. The relationship between these forms is given by the equation

$$\frac{[Fe(OH)Y^{-2}]}{[Fe(OH)_2Y^{-3}]} = 10^{9.5}[H^+]$$

According to this expression the complex with one hydroxyl group predominates at pH values below 9.5 while the complex with two hydroxyl groups predominates at pH values over 9.5.

One might expect that the coloured H_2O_2 complex is formed by the substitution of a perhydroxyl group for a hydroxyl group. However, if that were the case, K' would not depend but K would depend on the pH value of the solution. It seems therefore more likely that a hydroxyl group is replaced by a peroxide group O_2^{-2} according to

$$Fe(OH)Y^{-2} + O_2H^- = Fe(O_2)Y^{-3} + H_2O$$

or

$$Fe(OH)_2Y^{-3} + O_2H^- = Fe(O_2)(OH)Y^{-4} + H_2O$$

The fact that K does not depend on pH could also be explained by assuming that an aquo group of the Fe-EDTA complex is replaced by a perhydroxyl group.

It may be noted that the shape of the absorption curve is practically the same at pH values above and below 9.5. This indicates that irrespective of whether the Fe-EDTA component is a complex with one or two hydroxyl groups the colour of the hydrogen peroxide compound is the same. This colour seems to arise when the peroxide ion combines with the iron complex.

From the analytical point of view, the following remarks may be of some interest:

1. The coloured compound offers possibilities for determining iron photometrically in alkaline solutions where other metals can be effectively masked by EDTA.
2. The value of the stability constant is greater than 10^3. At pH values above 11 and using hydrogen peroxide in sufficient excess the reaction is practically complete.
3. The absorbance index is fairly large. At wavelengths of 500 mμ its numerical value is almost 10^3. The reaction seems to be particularly suitable for the determination of small amounts of iron in the presence of large amounts of copper. The absorbance curves in Fig. 1 illustrate the analytical possibilities.

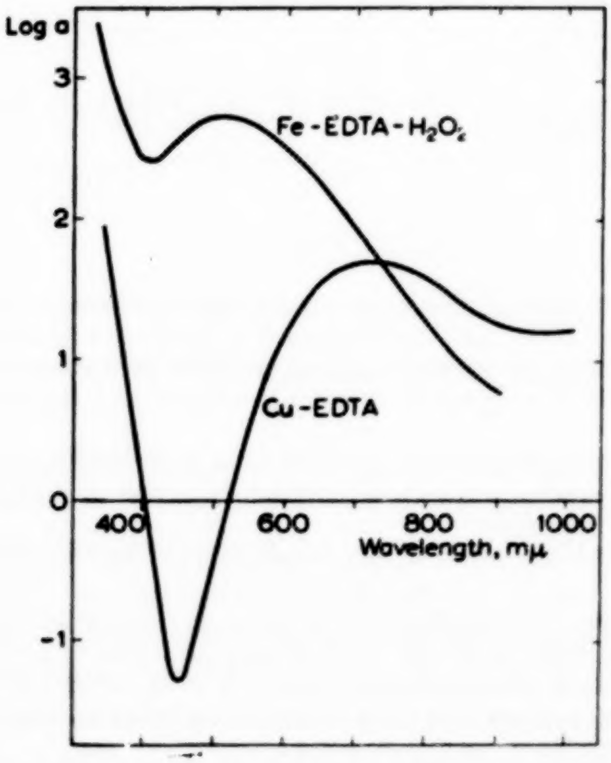

Fig. 1. The absorbance indices of Fe-EDTA-H_2O_2 and Cu-EDTA at pH ∼ 10.

It can be seen that the absorption maximum of the iron complex appears at about the same wavelength as the absorption minimum of the Cu-EDTA complex (copper forms no hydrogen peroxide complexes). The absorbance indices are given in logarithmic form, and the absorption of the iron compound is at 450 mμ about ten thousand times as great as that of the copper compound. The nickel complex has at this wavelength about the same absorbance index as the corresponding copper complex. The only metal that may be able to interfere, if present in large amounts, is cobalt. Hydrogen peroxide added to a solution of a cobalt salt gives in ammoniacal solution a blue colour which slowly changes into a red colour. However, these colours are not due to any compounds similar to the Fe-EDTA-H_2O_2 complexes described above. SCHWARZENBACH[5] has shown that the blue colour is caused by a cobalt hydroxyl complex $Co(OH)Y^{-2}$ and the red colour by CoY^-. We have been able to confirm his results. In other words, hydrogen peroxide acts in this case only as an oxidizing agent.

If cobalt is previously oxidized into its trivalent form, the addition of hydrogen peroxide does not cause any change in the colour; by using a blank the disturbing interference of cobalt in the determination of iron can thus be eliminated.

In Table III the results of some determinations of iron in the presence of other metals are given.

TABLE III

DETERMINATION OF IRON IN THE PRESENCE OF OTHER METALS

Metals present	*Volume ml*	*Absorbance*	*% Fe*	
			calc.	*obt.*
319.4 mg Cu, 0.518 mg Fe	25	0.148	0.162	0.160
319.4 mg Cu, 0.207 mg Fe	25	0.058	0.064	0.063
idem	25	0.059	0.064	0.064
319.4 mg Cu, 0.052 mg Fe	25	0.015	0.016	0.016
143.0 mg brass containing ca. 58% Cu, 39% Zn, 0.4% Sn, 0.7% Pb, 1.47% Fe	25	0.236	1.47	1.45
idem	25	0.237	1.47	1.45
82.2 mg of the same brass	25	0.136	1.47	1.45

Procedure

EDTA (as the disodium salt) is added in an amount at least equivalent to the heavy metals present to about 10 ml of the sample solution, and the solution is made about neutral with ammonia. Two ml 30% hydrogen peroxide and conc. ammonia (*ca.* 5 ml) until the pH value of the solution is 10.5-11 are added. The solution is diluted in a 25 ml flask until the mark and the absorbance is measured at a wavelength of 450 mμ.

Hydrogen peroxide has to be added before the solution is made strongly ammoniacal, since otherwise ferric hydroxide may be precipitated which can catalyze the decomposition of hydrogen peroxide and disturb the colour reaction.

A correction for a possible iron content of the reagents used can be applied if the absorbance of a blank is measured.

If coloured ions in very large concentrations are present, it may be advantageous not to use water as a reference, but a solution made as above without any addition of hydrogen peroxide. Then the results should be calculated using an absorbance index $\triangle a$ = the difference between the absorbance index of the violet peroxide compound and the absorbance index of the Fe-EDTA compound. At 450 mμ and pH 10.5 we found $\triangle a = 405 - 8 = 397$.

The brass sample was dissolved in a solution of nitric acid (1 : 1) + 1-2 g tartaric acid. The procedure given above was then followed. The theoretical value of the iron content in the brass sample was determined titrimetrically with $TiCl_3$ after the separation of iron as ferric hydroxide.

The accuracy of the analyses given in Table II is satisfactory.

ACKNOWLEDGEMENT

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SUMMARY

The reaction between iron(III)-ethylenediaminetetraacetate and hydrogen peroxide is studied; the formula and the stability constant of the strongly coloured product formed are determined. The reaction is used as basis of a method for the photometric determination of iron; the method seems particularly suitable for the analysis of samples very rich in copper.

RÉSUMÉ

La réaction entre Fe(III)-EDTA et l'eau oxygénée est étudiée. La formule et la constante de stabilité du complexe très coloré formé sont déterminées. Cette réaction peut être utilisée pour le dosage photométrique du fer. La méthode semble particulièrement recommandable pour l'analyse de substances renfermant beaucoup de cuivre.

References p. 545

ZUSAMMENFASSUNG

Die Reaktion zwischen Eisen(III)-äthylendiamintetraazetat und Wasserstoffperoxyd wurde untersucht. Die Formel des entstandenen farbigen Komplexes wurde festgestellt und die Stabilitätskonstante bestimmt. Die Reaktion dient als Grundlage einer Methode für die photometrische Bestimmung von Eisen; die beschriebene Methode scheint für die Analyse von Substanzen mit einem hohen Gehalt an Kupfer besonders geeignet.

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SUR LA STABILITÉ THERMIQUE DES ÉTALONS ANALYTIQUES. V*

par

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avec la collaboration technique de Mlles COLETTE WADIER ET YVETTE SERVIGNE

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Dans cette cinquième série, nous présentons une étude relative aux 12 corps suivants: biiodate de potassium, periodate de potassium, iodure d'ammonium, thiosulfate de baryum, chromate de potassium, thiocyanate de potassium, ferricyanure de potassium, ferrocyanure de potassium, acide benzoïque, hydroxy-8 quinoléïne, acide éthylènediamine-tétracétique, sel disodique de l'acide éthylènediamine-tétracétique.

Toutes ces substances ont été chauffées sur l'une des thermobalances à enregistrement photographique, avec échauffement linéaire à raison de 300° par heure et avec des poids de substance de l'ordre de 200 mg. Les spectres infrarouges ont été réalisés sur poudre avec de la vaseline comme agglomérant, entre 6 et 15 μ, sur le spectromètre Perkin-Elmer 12C, avec optique de sel gemme.

Biiodate de potassium

Ce corps est proposé de plus en plus comme étalon acidimétrique et comme agent oxydant. Il est anhydre et de poids constant jusqu'à 148°. Il s'échappe alors une molécule d'eau entre deux molécules de biiodate, sans que l'acide anhydro-iodique, signalé dans le quatrième mémoire de cette série, soit mis en évidence (Fig. 1). A partir de 180° et jusqu'à 370°, on observe un palier horizontal suivant lequel on a le mélange 2 $KIO_3 + I_2O_5$. L'anhydride iodique disparait alors par dissociation et par sublimation et vers 500° commence un court palier oblique suivant lequel il ne reste que de l'iodate de potassium, qui ne tarde pas d'ailleurs à se dissocier comme il est dit dans le troisième mémoire de cette série[1].

Le spectre infrarouge présente les fréquences suivantes: 744 (f), 765 (aF), 780 (f), 792 (tf), 820 (F), 832 (aF) cm^{-1}. Ce spectre est donc complètement différent de ceux donnés par les deux composants, lesquels au contraire présentaient des bandes communes.

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[1] C. DUVAL, *Anal. Chim. Acta*, 15 (1956) 224.

* Pour le quatrième mémoire de cette série, voir *Anal. Chim. Acta*, 16 (1957) 221.

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Métaperiodate de potassium

Ce sel est anhydre, bien sec tel qu'il sort du flacon et se montre stable jusqu'à 264° (Fig. 2). Il se détruit alors très lentement et la vitesse de décomposition s'accélère brusquement vers 350°. L'iodate de potassium formé quantitativement d'après RAMMELSBERG, se maintient entre 350 et 524°. Donc le point de fusion 582°, donné par CARNELLEY, ne peut pas s'appliquer au periodate, ni même à l'iodate. Au-dessus de 524°, s'observe un nouveau départ d'oxygène et l'on aboutit à l'iodure KI.

Le spectre infrarouge présente une bande très forte et unique pour 833 cm^{-1}.

Iodure d'ammonium

Ce corps est sec et anhydre et conserve un poids constant jusque vers 225° (Fig. 3). Il se sublime ensuite avec dissociation partielle au-delà de cette température et à 377° le creuset est complètement vide.

L'iodure d'ammonium ne présente pas de bande infrarouge dans cette région.

Thiosulfate de baryum

Ce sel sert de plus en plus d'étalon en iodométrie. Il se maintient sec et stable jusqu'à 84° (Fig. 4); il subit ensuite une décomposition et une réoxydation à partir de 447°, qui l'amène à l'état de sulfate de baryum.

Le spectre de ce corps a déjà été interprété. On y trouve les cinq bandes suivantes: 990 (F), 1009 (f), 1080 (F), 1108 (aF), 1122 (F) cm^{-1}.

Chromate de potassium

Le chromate de potassium ne change pas de poids d'une manière sensible jusqu'à 975°.

Ce sel présente un spectre infrarouge très net avec deux bandes, l'une à 853 (aF) et l'autre à 889 (TF) cm^{-1}. En solution aqueuse, ce sel présente une bande large entre 863 et 895 cm^{-1}.

Thiocyanate de potassium

Ce sel est très stable et se maintient inchangé jusque vers 480°. Il subit alors une décomposition lente en perdant du soufre et donnant du cyanure de potassium (Fig. 5).

Son spectre infrarouge, dans la région étudiée, présente les bandes suivantes: 740 (f), 745 (aF), 947 (aF), 971 (aF).

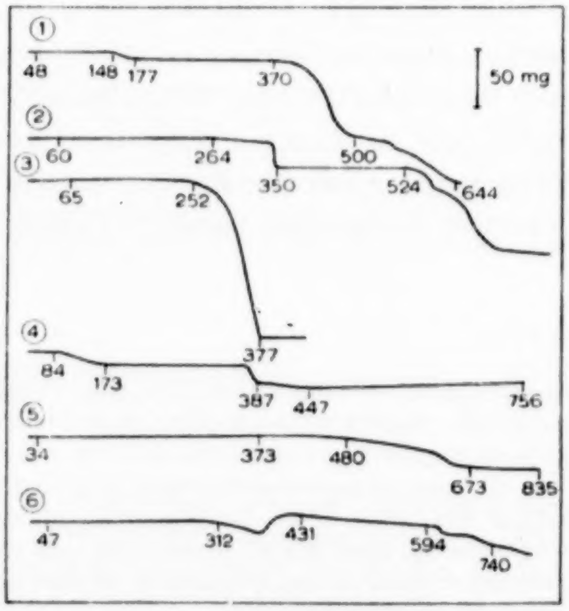

Fig. 1—6.

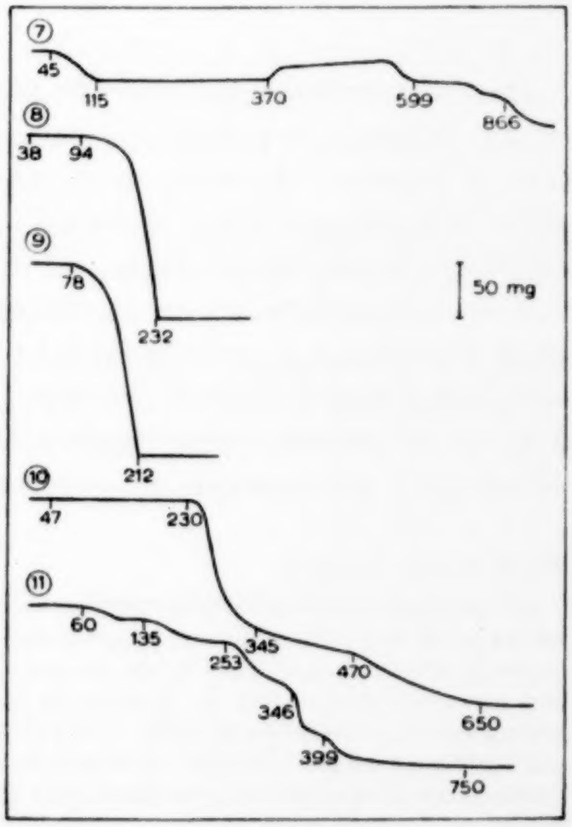

Fig. 7—11.

Ferricyanure de potassium

Il est anhydre, stable et conserve un poids constant jusqu'à 312° (Fig. 6). A partir de cette température commence une décomposition extrêmement compliquée, dans laquelle on observe à la fois une réoxydation et une perte de cyanogène.

Il n'y a pas de spectre infrarouge dans la région étudiée.

Ferrocyanure de potassium

Le ferrocyanure de potassium trihydraté est stable jusqu'à 45°. Les molécules d'eau s'échappent jusqu'à 115°. Après quoi, on observe le palier du sel anhydre jusque vers 370° (Fig. 7). Alors commence une oxydation du fer, puis il y a perte de cyanogène et l'on aboutit à un carbure de fer complexe.

Il n'y a pas de spectre infrarouge dans cette région.

Acide benzoïque

Ce corps est parfaitement sec quand on le sort du flacon. On peut le peser tel quel. Éventuellement, pour un séchage, il ne faudrait pas dépasser 94° car cet acide se sublime rapidement et au-dessus de 232° le creuset est vidé (Fig. 8).

Dans la région du sel gemme l'acide benzoïque présente un assez grand nombre de bandes à cause de la présence du noyau. Nous relevons notamment: 684 (F), 709 (F), 804 (aF), 812 (aF), 858 (f), 931 (TF), 1000 (aF), 1028 (F), 1073 (F), 1111 (aF), 1129 (F), 1180 (F), 1284 (TF), 1323 (F), 1425 (F) cm^{-1}.

Hydroxy-8 quinoléïne

L'hydroxy-8 quinoléïne ou oxine est un corps généralement sec que l'on peut peser directement. Elle ne perd pas de poids avant 78°, température à laquelle elle commence à se sublimer. Le creuset est vide à 212° (Fig. 9).

Dans son spectre infrarouge nous relevons les bandes suivantes: 711 (F), 743 (aF), 781 (F), 788 (f), 808 (f), 819 (F), 864 (f), 896 (f), 972 (f), 1060 (f), 1096 (aF), 1167 (f), 1207 (aF), 1221 (aF), 1274 (F), 1405 (aF), 1504 (aF).

Acide éthylènediamine-tétracétique (EDTA)

C'est un corps stable jusqu'à 230°, parfaitement sec et que l'on peut peser directement. Au-dessus de cette température il se sublime et se détruit et le creuset est vide vers 650° (Fig. 10).

On relève dans son spectre les bandes suivantes: 812 (f), 863 (f), 908 (aF), 965 (F), 1009 (aF), 1041 (f), 1056 (aF), 1096 (aF), 1214 (aF), 1235 (aF), 1264 (aF), 1287 (aF), 1325 (aF), 1350 (aF) cm^{-1}.

Sel disodique de l'acide éthylènediamine-tétracétique (versène, complexon, trilon B)

Ce sel ne contient pas un nombre de molécules d'eau de cristallisation fixe. Il est réputé posséder 2 H_2O; le produit qui nous a servi en contenait à peine 1; c'était donc un mélange. En vue d'une pesée précise, il faut déshydrater complètement le sel entre 100 et 120° (Fig. 11). Déjà à 135° il commence à perdre du poids et l'on arrive vers 750° à du carbonate de sodium partiellement dissocié.

Le spectre infrarouge présente quelques bandes communes avec le précédent. Nous avons pu relever les bandes suivantes: 816 (F), 900 (F), 920 (F), 940 (aF), 958 (aF), 983 (aF), 1019 (F), 1056 (F), 1122 (F), 1193 (aF), 1237 (aF), 1267 (aF), 1296 (aF), 1319 (aF), 1370 (f), 1402 (f) cm^{-1}.

RÉSUMÉ

Les auteurs ont étudié la stabilité thermique de douze substances servant comme étalons en chimie analytique et pour certaines d'entre elles, ils ont enregistré le spectre infrarouge dans la région du sel gemme. Seul, le sel disodique de l'EDTA doit être complètement déshydraté pour que l'on puisse faire sa pesée d'une façon sûre.

SUMMARY

The authors have studied the thermal stability of 12 substances used as standards in chemical analysis, and for some of them they have recorded the infrared spectra in the rock-salt region. The disodium salt of EDTA is the only one which must be completely dehydrated in order to insure accurate weighing.

ZUSAMMENFASSUNG

Die Verfasser haben die Hitzebeständigkeit von zwölf Substanzen die in der analytischen Chemie als Standard dienen, untersucht und für einige von ihnen das Ultrarotspektrum im Steinsalzbereich aufgenommen. Nur das EDTA-Dinatriumsalz muss vollständig entwässert sein um mit Sicherheit gewogen ~~zu~~ werden können.

Reçu le 12 janvier 1957

ANALYSIS OF ADENINE AND INOSINE NUCLEOTIDES

by

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The methods so far described for separating and analysing mixtures of ATP* and its organic and inorganic derivatives do not always allow a complete or satisfactory analysis of this group of substances.

Procedures have therefore been worked out permitting the accurate analysis of such mixtures both in pure solutions and in biological materials. These are:

A) Chromatography
  1) on filter paper: a) with the ascending technique
    b) with the descending technique
  2) on paper roll
  3) on cellulose column
B) Electrophoresis
  1) on filter paper
  2) on cellulose column

EXPERIMENTAL

Materials

Adenosinetriphosphate, sodium salt (ATP 4 Na): Boehringer and Söhne.
Adenosinediphosphate, barium salt (ADP 2 Ba): Sigma Chemicals (St. Louis, U.S.A.).
Muscle adenylic acid: Pabst Laboratories (Milkwaukee, U.S.A.).
Yeast adenylic acid, inosine and hypoxanthine: Fluka A.G., Chemische Fabrik (Buchs/S.G., Switzerland).
Inosine-mono-, -di- and -triphosphate barium salts: Bios Laboratories (New York, U.S.A.).
Adenine and adenosine: Light and Co. (Poyle, England).
All barium salts were transformed into sodium salts according to HAWK *et al.*[1]

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* The following abbreviations are used:

ATP = adenosinetriphosphate
ADP = adenosinediphosphate
AM-5-P = adenosinemono-5-phosphate (muscle adenylic acid)
AM-3-P = adenosinemono-3-phosphate (yeast adenylic acid)
AS = adenosine
Ad = adenine
ITP = inosinetriphosphate
IDP = inosinediphosphate
IMP = inosinemonophosphate
Is = inosine
Hx = hypoxanthine
PP = inorganic pyrophosphate
P = inorganic orthophosphate
TCA = trichloroacetic acid

Methods

A. *Chromatography*

1) *Paper chromatography*

Solvent: *n*-propanol—H_2O—100%TCA—NH_3 22° Bé (75 : 20 : 5 : 0.3).

The mixture containing not more than 100 μg each of Hx, Ad and derivatives, 10 μg each of inorganic phosphates is applied at a distance of 5 cm from the end of a 6 × 48 cm strip of unwashed Munktell CRH 100 paper. The paper is run for 20-22 hours in ascending chromatography or for 36-40 hours in descending chromatography.

After drying in a fume chamber at room temperature, the organic derivatives are located by the aid of a Mineralight short wave U.V. lamp, a filter SL 2537 (Ultraviolet Products, South Pasadena, California) being used, and appear as non-transparent bluish spots. If a permanent record or a more sensitive detection is required the paper is photographed in ultraviolet light as described by MARKHAM AND SMITH[2].

The inorganic derivatives are located by spraying the paper with a solution of 1.25% ammonium molybdate in 0.5*N* H_2SO_4 (Reagent A) and, after the paper has dried, with a newly prepared solution of 0.5% ascorbic acid in water (Reagent B).

Contact with unprotected glass surfaces during preparation and storage has to be strictly avoided for both reagents.

Orthophosphate develops after few minutes a bright blue color, while PP takes about 90 minutes to appear as a dark blue spot. The identification of the separated compounds is carried out by reference to the spots obtained from a known mixture in a parallel run or, the R_F values being remarkably constant (Table I), by measuring the R_F of each spot.

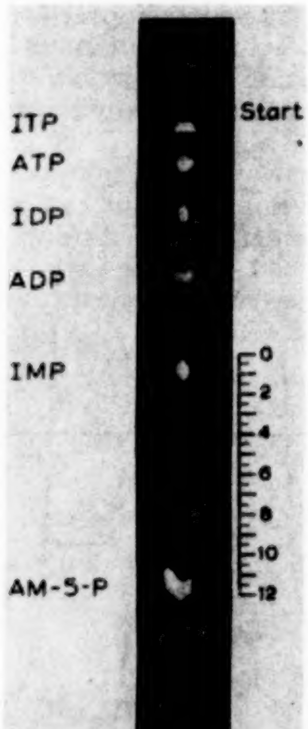

Fig. 1. Separation by descending chromatography on Munktell CRH 100 paper of a mixture containing 75 μg each of ATP and ADP, 80 μg each of adenosine IDP, ITP, IMP, 70 μg of adenine, 90 μg AM-5-P. Solvent: propanol—H_2O—100% TCA—NH_3 22° Bé (75:20:5:0.3) 36 hours. The photograph was taken in ultraviolet light according to MARKHAM AND SMITH[2].

Quantitative determination. No breakdown of the pure compounds during chromatography was observed when these were run separately. For this reason and because the spots are sharply defined and without tailing, densitometry of the separated spots was usefully applied to the quantitative estimation of the components of the mixture.

TABLE I

R_F VALUES OF ADENINE AND INOSINE NUCLEOTIDES AND OF INORGANIC PHOSPHATES IN *n*-propanol—H_2O—100% TCA—NH_3 22° Bé (75:20:5:0.3) at 22°C

ATP	0.03
ADP	0.12
AM-5-P	0.41
AM-3-P	0.41
AS	0.59
Ad	0.69
ITP	0.02
IDP	0.07
IMP	0.22
Is	0.38
Hx	0.24
PP	0.24
P	0.65

For this purpose duplicate separations for each samples are run and dried in the usual way, one being used for determining the organic and the other for the inorganic compounds. The first one is sprayed on both surfaces with a solution of 2% orcine in 85 parts 2*N* HCl and 10 parts 95% ethanol and each surface is allowed to dry at room temperature after having been sprayed. It is then put in an oven at 85-90°C for 2-3 minutes. The spots appear green on pale pink background and after 3 hours their absorbancy is determined with a densitometer.

The paper selected for the determination of the inorganic phosphates is sprayed on both surfaces with reagent A, allowing it to dry at room temperature after each spraying and then sprayed in an identical way with reagent B.

The spot corresponding to P appears within few minutes and is read in a densitometer 8 hours after spraying while the spot of PP develops in about 1½ hours and is read 20 hours after spraying.

When the described procedure is correctly applied under uniform conditions the recoveries are constant and reproducible within ± 2%.

Calculation may be based on the standard reference curves drawn from data as obtained with solutions of the single pure compounds.

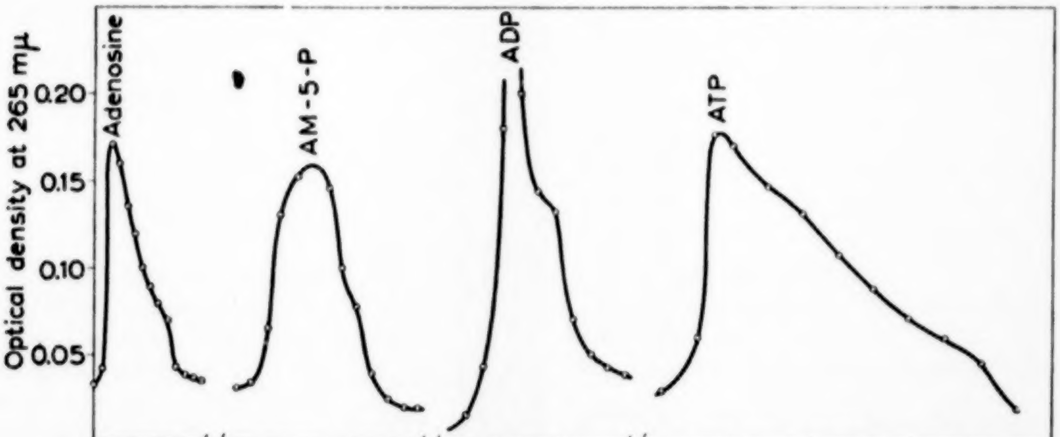

Fig. 2. Separation by chromatography on a Grycksbo paper roll of adenine nucleotides; the mixture contained 10 mg of each substance. Flow rate 30 ml/h. Solvent *n*-propanol—H_2O—100% TCA—NH_3 22° Bé (75:20:5:0.3).

The determination of ATP, ITP and their organic derivatives can equally well be obtained by elution after the chromatographic run. The spots are eluted with water, as described by **Brimley and Barret**[3], at a flow rate of 0.5 ml/h; in each case 3 ml eluate were collected and the AS and Is compounds determined by the method of **Albaum and Umbreit**[4]. Calculations may be based on the standard reference curves.

References p. 554

2) *Chromatography on paper roll*

The solvent used was the same as for paper chromatography. A Grycksbo paper roll, type LKB 3391, was prepared according to HAGDAHL AND DANIELSSON[5]. A mixture containing 10 mg each of ATP, ADP, AM-5-P and AS dissolved in 20 ml of the solvent was applied, the flow rate of the solvent being then adjusted to 30 ml/h. The effluent was collected in 6 ml fractions and determinations carried out by the method of ALBAUM AND UMBREIT[4]. The elution curves are shown in Fig. 2.

The recovery was quantitative.

3) *Chromatography on a cellulose column* has been attempted as a preliminary step to column electrophoresis.

A column of 3.5 × 50 cm packed with cellulose powder Whatman B quality, Standard grade was used. The solvent was ammonium formate pH 3, 0.05*M*.

A mixture containing 1.5 mg each of ATP, ADP, AM-5-P and AS, and 1 mg Ad dissolved in 3 ml of water was applied to the column and eluted at a flow rate of 50 ml/h. The effluent was collected in 9 ml fractions and the extinction coefficients were measured in a Beckman DU spectrophotometer at 265 mµ. The identification of the compounds was carried out with the help of paper chromatography or electrophoresis. When necessary the fractions to be analysed were evaporated under reduced pressure at 35°C until suitable concentration for paper electrophoresis or chromatography was reached.

The elution curves are represented in Fig. 3.

Only four peaks are seen since the separation of ATP from ADP is not obtained.

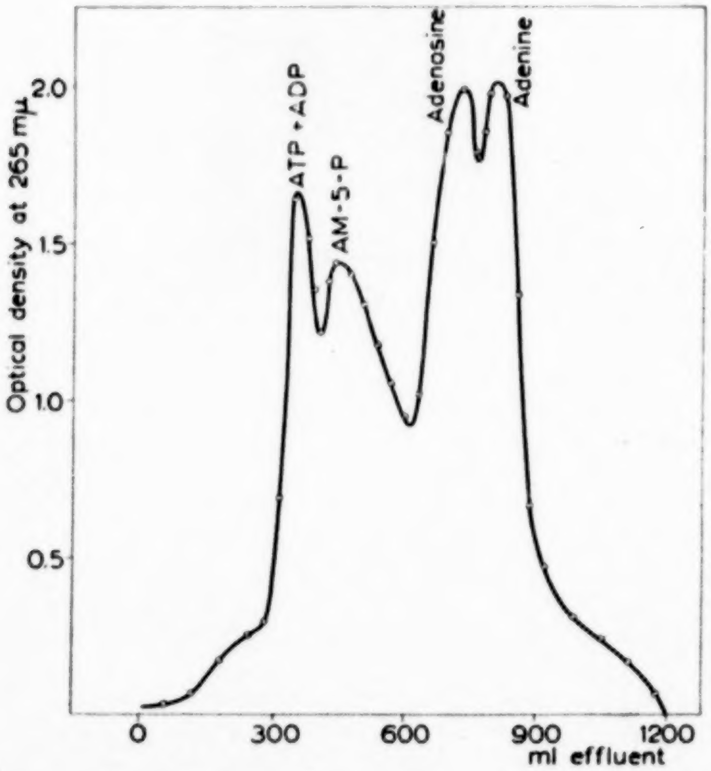

Fig. 3. Chromatography on a cellulose powder column of a mixture containing 1.5 mg each of ATP, ADP, AM-5-P and adenosine, and 1 mg adenine.
Solvent ammonium formate buffer pH 3.01, 0.05*M*. Flow rate 30 ml/h.

B. Electrophoresis

1) *Paper electrophoresis*

A mixture containing up to 200 µg each of ATP and ADP, 250 µg of AM-5-P and 50 µg of AS and Ad was applied, at a distance of 20 cm from the cathode, in one spot to a strip (8 × 40 cm) of Munktell 20 paper. Equal amounts were reached in the separation of inosine derivatives.

The electrophoresis was run in ammonium formate buffer pH 3, 0.05*M*. A potential of 300 V was applied giving a current of 0.6 mA/cm width.

The ends of the strips were cut off at the end of the run in order to prevent the spread of the liquid from the buffer solution into the paper, and the paper was dried. The spots were located and identified as described for paper chromatography.

The separation of the mixture of ATP derivatives is shown in Fig. 4.

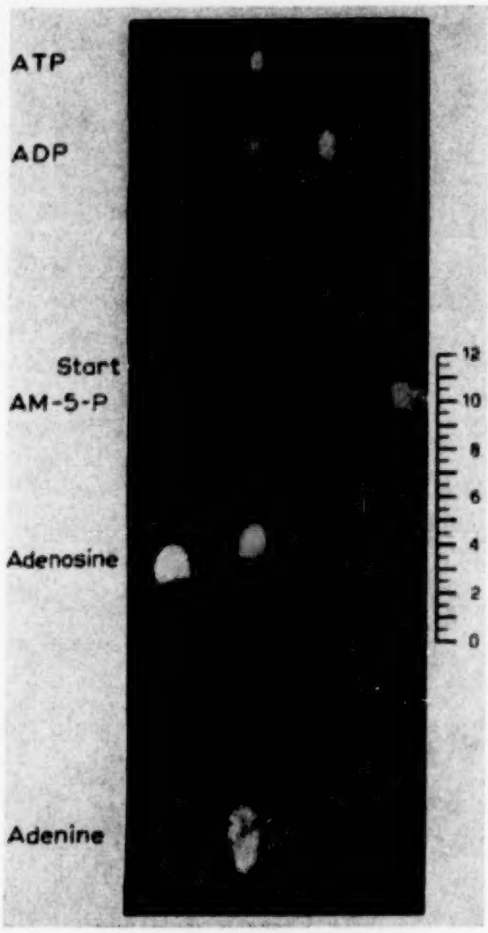

Fig. 4. Separation by electrophoresis on Munktell 20 paper of different mixtures of ATP (100 μg), ADP (100 μg), AM-5-P (100 μg), adenosine (50 μg), adenine (50 μg). Ammonium formate buffer 0.05M pH 3.02, 300 V, 20 mA/cm during 8 hours. The photograph was taken in ultraviolet light according to Markham and Smith[2].

The migration of PP is so fast, as compared to that of the other components of the mixture, that a duplicate proof, (not more than 15 μg each of P and PP), running only 3 hours, is usually carried out when identification and determination of PP is required.

Attempts of separation between AM-5-P and AM-3-P have been unsuccessfull.

Quantitative determination. For this purpose the mixture was applied to the paper with an Agla micrometer syringe (Burroughs Wellcome Ltd). The electrophoresis is run in the usual way and the spots of ATP and of its organic derivatives are eluted with water as described by Brimley and Barret[3] at a flow rate of 0.5 ml/h; in each case 7-8 ml eluate were collected in a graduate tube.

The absorbancy of the eluate at 265 mμ was determined in a Beckman spectrophotometer, the fluid collected under the same conditions from a similar piece of filter paper from the same strip being used as a blank. Calculation may be based on the standard reference curves.

The determination of the inorganic phosphate is carried out as described in a previous section, the only difference being that the spots develop their colour in a shorter time. The spot corresponding to P is read therefore after 120 minutes and that corresponding to PP after 12 hours.

2) *Cellulose column electrophoresis*

The apparatus and the technical details employed were those of Flodin and Kupke[6]. 0.05M ammonium formate, pH 3, was used as buffer.

A mixture containing up to 2 mg of each compound in 3 ml buffer was put on the top of the column (3.5 × 50 cm) of cellulose powder. Before the current was applied the mixture was displaced 20-25 cm down the column by allowing a 190 ml of the buffer to flow through the column. The top of the column was then connected to the cathode, the bottom to the anode and a potential of 300 V, corresponding to a current of 14 mA, applied for 18 h. The elution, determination and identification of the separated compounds were performed as described for cellulose column chromatography.

The separation of a mixture of ATP and its derivatives is shown in Fig. 5.

Quantitative recoveries have been obtained.

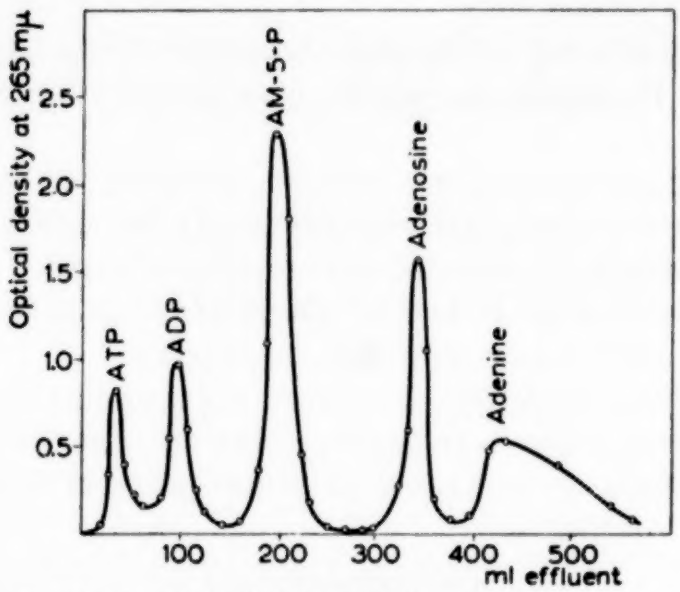

Fig. 5. Separation by column electrophoresis of a mixture containing 1.5 mg each of ATP, ADP, adenosine and adenine, and 2 mg AM-5-P. Whatman cellulose powder. Ammonium formate buffer pH 3.02, 0.05*M*. 300 V; 14 mA for 18 hours.

C. Application to biological material

Liver and kidney homogenates were prepared according to LE PAGE *et al.*[7] and mixtures of Ad and Is derivatives were added to the homogenate so that in each sample the final homogenate concentration was 2.5% and the concentration of each added substance was 0.5%.

Immediately after addition of the substrates the proteins were precipitated by heating, or by addition of TCA, and the chromatography or electrophoresis carried out with a convenient aliquot of the supernatant.

The results were identical to those obtained with solutions of the pure compounds.

DISCUSSION

The methods here described allow the separation and determination of mixtures of adenylic and inosinic derivatives by different ways so that a convenient choice is possible in adopting the most convenient to one's aims.

Paper chromatography is remarkable for its simplicity and constancy of results. The ascending technique allows a quicker separation, but the R_F values of ATP, ADP, ITP, IDP are so close to each other that a satisfactory separation when all these compounds are present is hardly possible. Owing to the well delimited spots obtainable, an ascending run is preferred when the quantitative determination of inorganic phosphates is required[8]. The best resolutions of mixtures containing AS and Is polyphosphates are obtained by descending chromatography. This technique is therefore preferred for qualitative purposes and for the elution of the spots.

A first advantage of paper electrophoresis on chromatography is the short duration of the run. The separations obtained are excellent and reproducible. Care must however be taken in adjusting the pH of the buffer, the resolution of the organic di- and triphosphates being highly dependent on the pH. Also the densitometric determination of inorganic phosphates is safer after electrophoresis since no background coloration is formed in this case. Background colour does however not develop even on chromatograms if a fine nebulyser is used for spraying and the paper is only moderately moistened and if after spraying care is taken not to expose the paper to intense light for longer periods of time.

The molybdate colour reaction in mixtures separated by paper electrophoresis develops on the same pattern as discussed in a previous paper[8], but all the sequency of events takes place in a shorter time.

For the determination of Ad and Is derivatives, the elution of spots is preferred for its greater simplicity. The results are equally good after chromatography and electrophoresis.

Mixtures containing greater amounts of each substance can be separated by paper roll chromatography and by column electrophoresis. In the latter method, however, the determination of substances is easier and moreover the separated compounds are more easily obtained in a dry form since they are dissolved in a volatile buffer. This method can therefore be used also for micropreparative purposes.

The methods have proved highly satisfactory when applied to biological materials also in experiments where a high homogenate/substrate ratio had been employed so as to ascertain that substances contained in tissue preparations do not hinder the separation.

ACKNOWLEDGEMENT

This investigation was aided by grants from the Rockefeller Foundation, to which grateful acknowledgement is made.

SUMMARY

Different methods are described for the separation and determination of adenine, hypoxanthine, adenosine, inosine and their phosphorylated derivatives, and inorganic ortho- and pyrophosphate: 1) chromatographic procedures on paper, cellulose powder column and paper roll, 2) electrophoretic procedures on paper and cellulose powder column. These procedures have been successfully applied to biological materials and some of them can be used for micropreparative purposes.

RÉSUMÉ

Différentes méthodes sont décrites pour la séparation et le dosage de l'adénine, de l'hypoxanthine, de l'adénosine, de l'inosine et de leurs dérivés phosphorylés, ainsi que des ortho- et pyrophosphates inorganiques: 1) procédés chromatographiques sur papier, sur colonne de poudre de cellulose et sur rouleau de papier; 2) procédés d'électrophorèse sur papier et sur colonne de poudre de cellulose. Ces méthodes ont été appliquées avec succès en biologie et quelques-unes d'entre elles peuvent être utilisées pour des micropréparations.

ZUSAMMENFASSUNG

Verschiedene Methoden zur Trennung und Bestimmung von Adenin, Hypoxanthin, Adenosin, Inosin und phosphorylierten Derivaten, und von anorganischem Ortho- und Pyrophosphat werden beschrieben: 1) Chromatographische Verfahren auf Papier, Zellulosepulversäule und Papierrolle, 2) Elektrophoretische Verfahren auf Papier und Zellulosepulversäule. Diese Verfahren wurden erfolgreich für biologisches Material angewendet und einige von ihnen können für mikropräparative Zwecke dienen.

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CHROMATOGRAPHIE INORGANIQUE SUR PAPIER

ÉTUDE DE LA VARIATION DE R_F AVEC LA CONCENTRATION DE HCl EN MELANGES (1 : 1) *n*-BUTANOL + HCl

par

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M. LEDERER a réalisé avec la collaboration de l'auteur, un travail[1] sur la détermination des valeurs de R_F de Be, Ge, Ga et In, en utilisant des mélanges (1 : 1) de *n*-butanol + HCl, et en faisant varier la concentration de HCl. On a ainsi établi la concentration optima de HCl pour la séparation de ces 4 éléments.

A la suite des résultats encourageants obtenus, et du fait que le seul mélange *n*-butanol + HCl 1*N* a été systématiquement expérimenté par M. LEDERER[2], nous avons pris la résolution d'effectuer le présent travail pendant notre séjour à l'Institut du Radium, à Paris.

Les valeurs obtenues ont été utilisées pour tracer les courbes de variation de R_F avec la concentration de HCl. L'observation de ces courbes nous permet de tirer d'intéressantes conclusions comme nous le verrons en temps opportun.

PARTIE EXPÉRIMENTALE GÉNÉRALE

Procédé utilisé — Chromatographie ascendante.

Papier — Whatman nr. 1 pour chromatographie.

Éluants — Mélanges (1 : 1) de *n*-butanol avec HCl 1, 2, 4, 6, 8, 10 et 12*N*. Seuls les trois premiers mélanges ont deux phases (phase alcoolique et phase aqueuse).
Les autres forment une seule phase.

Solutions — Pour chaque ion, nous avons préparé des solutions sensiblement molaires (en utilisant HCl *N* comme solvant) à partir, autant que possible, des chlorures ou des hydroxydes.

Exécution des essais

Pour chaque série d'essais, nous avons préparé les sept mélanges d'éluants qui étaient conservés dans des flacons de 6 litres fermés pendant la nuit pour permettre à l'équilibre de s'établir.

Par ailleurs, on a tracé sur les feuilles de papier à 3 cm du bord inférieur de la feuille, des cercles de 5 mm de diamètre, éloignés de 3 cm les uns des autres. On a placé, à l'aide d'un capillaire, au centre de chaque cercle, les gouttes des solutions à essayer, de telle façon qu'elles occupent, après expansion, la surface du cercle.

Après séchage à l'air (60 minutes), les feuilles sont roulées de façon à former des cylindres, lesquels sont alors introduits dans les flacons et ceux-ci fermés de nouveau. Après 15 heures on enlève les feuilles, on marque les fronts des liquides et on laisse sécher à l'air. Les feuilles sont alors découpées en bandes, et on révèle les taches avec les réactifs appropriés. Dans le cas des isotopes radioactifs la révélation est faite à l'aide d'un compteur Geiger, en parcourant toute la bande, centimètre par centimètre, et en mesurant l'activité de chaque section. En traçant le radiochromatogramme, on détermine facilement la position de l'élément chromatographié.

Chaque série d'essais est constituée par 7 feuilles de papier avec tous les éléments d'un groupe du tableau périodique. Chaque feuille est traitée avec un éluant, tous les traitements étant simultanés pour éviter des différences dues à des variations de température.

Presque tous les éléments ont été chromatographiés au moins deux fois en plusieurs jours. Les valeurs de R_F présentées sont ainsi les moyennes d'au moins deux mesures.

Valeurs de R_F

Les valeurs de R_F ont été calculées en considérant comme hauteur d'ascension la distance de la ligne droite initiale au centre de la tache révélée. On indique aussi les valeurs de R_F référents aux bords supérieur et inférieur de la tache, bien que ces chiffres n'aient pas une très grande valeur, puisqu'ils dépendent de la concentration de la solution et de la surface de la tache initiale. Cependant dans notre cas, comme les conditions initiales sont semblables, la valeur relative de ces chiffres a un intérêt, car elle nous permet de vérifier si les taches sont longues ou courtes.

Révélation

(1) Pulvérisation avec solution de periodate de fer[3].
(2) Compteur Geiger.
(3) Pulvérisation avec solution concentrée de cobaltinitrite de sodium.
(4) Immersion en solution alcoolique-ammoniacale de 8-hydroxy-quinoléine.
(5) Pulvérisation avec solution ammoniacale de rhodizonate de sodium.
(6) Pulvérisation avec solution aqueuse de tanin.
(7) Immersion en solution alcoolique d'alizarine S et exposition aux vapeurs d'ammoniaque.
(8) Pulvérisation avec thiocyanate d'ammonium et chlorure stanneux.
(9) Pulvérisation avec ammoniaque.
(10) Pulvérisation avec thiourée.
(11) Pulvérisation avec solution de chlorure stanneux.
(12) Pulvérisation avec solution aqueuse de H_2S.
(13) Pulvérisation avec solution de sulphure d'ammonium.
(14) Pulvérisation avec solution alcoolique de curcuma.
(15) Pulvérisation avec solution d'iodure de potassium.
(16) Pulvérisation avec solution alcoolique de phénylfluorone.
(17) Pulvérisation avec réactif de Nessler.
(18) Pulvérisation avec solution de nitromolybdate d'ammonium et benzidine, et exposition aux vapeurs d'ammoniaque.
(19) Pulvérisation avec solution chloroformique de dithizone.
(20) Compteur de particules α.
(21) Immersion en solution de nitrate d'argent et exposition à la lumière solaire.
(22) Tache colorée révélant sa position.
(23) Pulvérisation avec solution de ferrocyanure de potassium.

Éléments non-essayés

Nous n'avons pas essayé les gaz (H, He, O, Ne, A, Kr, Xe, Rn), les éléments radioactifs que nous n'avons pas pu nous procurer (At, Fr et les transuraniens), les éléments que nous n'avons pas réussi à révéler sur le papier (F, Os), et le carbone.

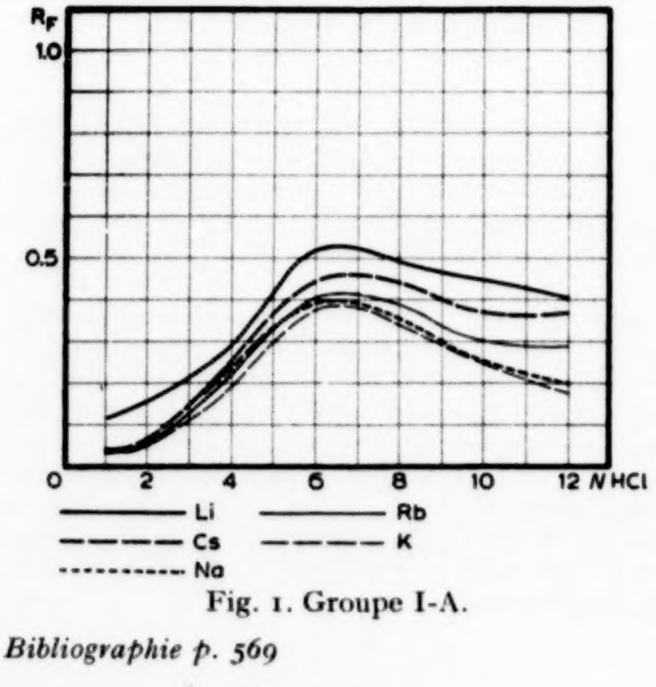

Fig. 1. Groupe I-A.

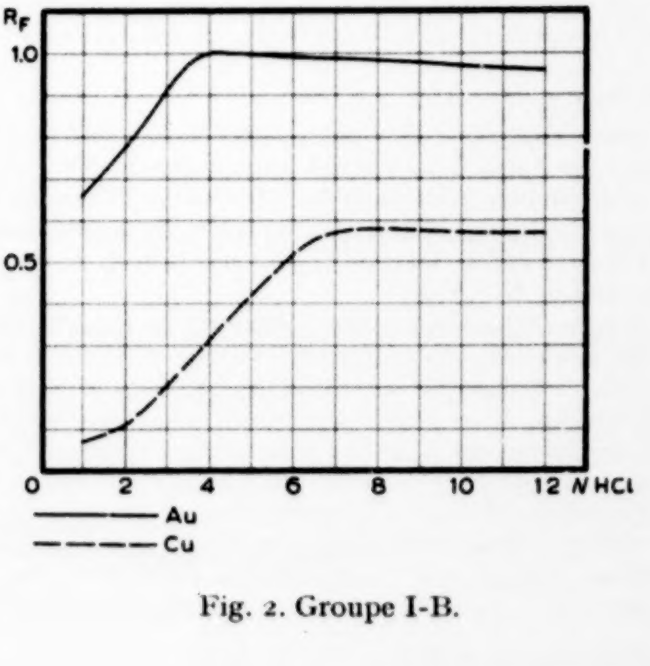

Fig. 2. Groupe I-B.

GROUPE I

A — Li, Na, K, Rb, Cs (Fig. 1)

ions/[HCl]	1N	2N	4N	6N	8N	10N	12N	Révél.
Li^{+}	0.12 ± 0.04	0.16 ± 0.06	0.29 ± 0.08	0.52 ± 0.08	0.49 ± 0.07	0.45 ± 0.07	0.41 ± 0.06	(1)
Na^{+}(^{22}Na)	0.04	0.06	0.25	0.39	0.35	0.25	0.20	(2)
K^{+}	0.03 ± 0.03	0.05 ± 0.03	0.19 ± 0.06	0.38 ± 0.05	0.34 ± 0.05	0.25 ± 0.07	0.18 ± 0.08	(3)
Rb^{+}	0.04 ± 0.03	0.06 ± 0.04	0.22 ± 0.05	0.41 ± 0.04	0.39 ± 0.04	0.30 ± 0.04	0.29 ± 0.03	(3)
Cs^{+}	0.04 ± 0.03	0.06 ± 0.04	0.25 ± 0.04	0.45 ± 0.05	0.44 ± 0.04	0.37 ± 0.04	0.37 ± 0.04	(3)

B — Cu, Ag, Au (Fig. 2)

ions/[HCl]	1N	2N	4N	6N	8N	10N	12N	Révél.
Cu^{+2}	0.07 ± 0.03	0.11 ± 0.04	0.31 ± 0.05	0.52 ± 0.05	0.58 ± 0.05	0.57 ± 0.04	0.57 ± 0.04	(4)
Ag^{+}	0	0	0	0	0	0	0	(13)
Au^{+3}	0.66 ± 0.02	0.78 ± 0.03	1.00 ± 0.02	0.99 ± 0.01	0.99 ± 0.01	0.97 ± 0.02	0.96 ± 0.02	(11)

GROUPE II

A — Be, Mg, Ca, Sr, Ba, Ra (Fig. 3)

ions/[HCl]	1N	2N	4N	6N	8N	10N	12N	Révél.
Be^{+2}	0.12 ± 0.04	0.18 ± 0.04	0.44 ± 0.04	0.59 ± 0.04	0.59 ± 0.04	0.52 ± 0.04	0.42 ± 0.04	(4)
Mg^{+2}	0.03 ± 0.01	0.06 ± 0.02	0.23 ± 0.04	0.43 ± 0.04	0.40 ± 0.04	0.35 ± 0.04	0.29 ± 0.04	(4)
Ca^{+2}	0.02 ± 0.01	0.03 ± 0.02	0.18 ± 0.03	0.34 ± 0.04	0.33 ± 0.03	0.23 ± 0.04	0.18 ± 0.03	(4)
Sr^{+2}	0 ± 0.01	0.01 ± 0.02	0.08 ± 0.02	0.30 ± 0.04	0.25 ± 0.04	0.16 ± 0.04	0.10 ± 0.03	(5)
Ba^{+2}	0 ± 0.02	0.01 ± 0.01	0.08 ± 0.02	0.17 ± 0.07	0.09 ± 0.09	0.05 ± 0.05	0.03 ± 0.03	(5)
Ra^{+2}(AcX)	0	0	0.11	0.14	0.08	0.05	0.02	(2)

B — Zn, Cd, Hg (Fig. 4)

ions/[HCl]	1N	2N	4N	6N	8N	10N	12N	Révél.
Zn^{+2}	0.60 ± 0.03	0.71 ± 0.02	0.98 ± 0.02	1.00 ± 0.02	0.89 ± 0.03	0.84 ± 0.05	0.75 ± 0.05	(4)
Cd^{+2}	0.52 ± 0.04	0.67 ± 0.02	0.97 ± 0.01	0.99 ± 0.01	0.98 ± 0.02	0.91 ± 0.03	0.80 ± 0.04	(13)
Hg^{+2}	0.79 ± 0.04	0.84 ± 0.03	1.00 ± 0.01	0.99 ± 0.01	0.98 ± 0.03 (queue jusqu'à 0.89)	0.90 ± 0.03	0.83 ± 0.04	(13)

Observations sur les résultats (Groupe I)

A_1 — Avec aucun des éluants essayés, il n'a pas été possible de séparer Na de K.

A_2 — La séparation de Cs-Rb paraît être possible avec HCl 12*N*, puisqu'il y a une différence de 0.08 entre les valeurs de R_F. Toutefois nous n'avons pas essayé la séparation.

A_3 — Avec le potassium, on observe quelques taches allongées qui s'accentuent dans les solutions 10 et 12*N*, probablement en raison d'une diminution de la solubilité de KCl dans HCl.

A_4 — Il est curieux de noter qu'il y a une inversion à partir de K, c'est-à-dire, les valeurs de R_F vont en diminuant du Li jusqu'au K, mais après cela elles montent pour Rb et plus encore pour Cs. S'il y avait une régularité comme dans le groupe II-A, nous pourrions supposer que l'augmentation du rayon ionique déterminerait l'abaissement des R_F. Toutefois cette explication, qui convient très bien pour le groupe II-A, ne peut pas s'appliquer ici. Nous n'avons pas pour le moment d'hypothèse satisfaisante.

B_1 — Les taches de Cu sont approximativement circulaires tandis que celles de Au sont aplaties, du fait qu'elles sont toujours sur le front du liquide.

B_2 — L'*argent* peut se séparer aisément des deux autres éléments, puisqu'il précipite sous forme de AgCl qui reste au point d'application.

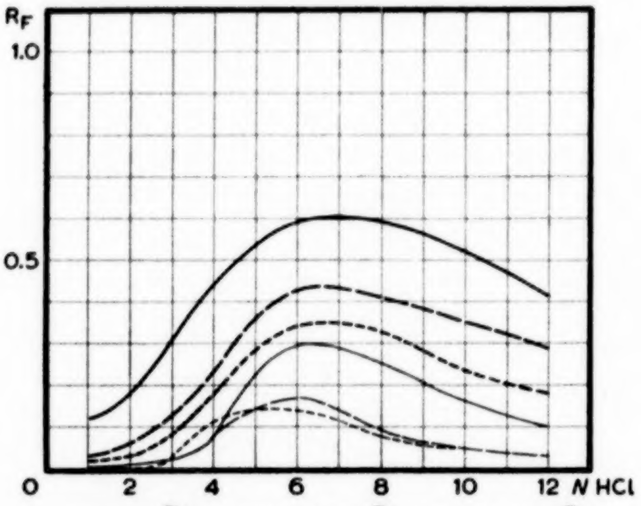

Fig. 3. Groupe II-A.

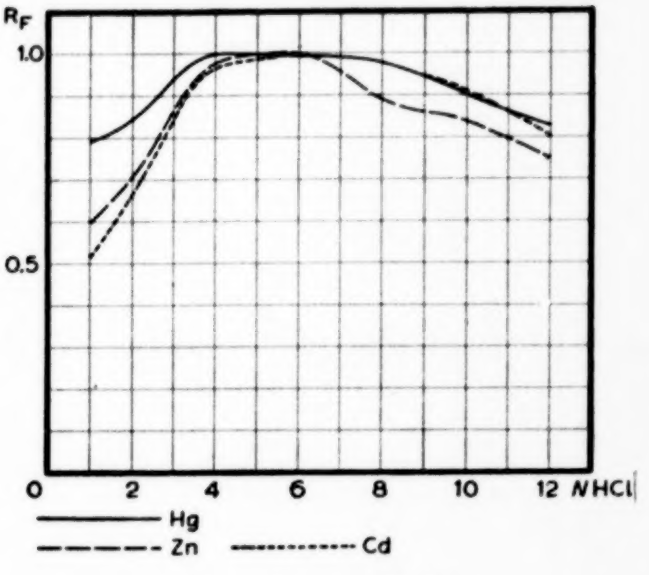

Fig. 4. Groupe II-B.

Observations sur les résultats (Groupe II)

A_1 — Le *magnésium* se sépare de Ca à partir de HCl 6*N*, tandis que des autres il se sépare déjà à partir de 4*N*.

A_2 — C'est à 4*N* que le *calcium* se sépare le mieux de Sr et Ba.

A_3 — Le *strontium* jusqu'à 4*N* présente les mêmes valeurs que Ba, mais à 6*N* il est déjà complètement séparé; à 8*N*, la séparation de cet élément est la meilleure ($\triangle\ R_F = 0.16$).

A_4 — Le *baryum* commence, à partir de 8*N*, à former une grande comète qui s'étend jusqu'à l'origine. Cela est dû à la faible solubilité de $BaCl_2$ dans HCl concentré.

A_5 — Le *radium* présente des valeurs de R_F très semblables à celles de Ba; on note uniquement à 4 et 8*N* de petites différences.

Comme ces petites différences pourraient être utilisées pour une séparation possible de Ra et Ba en milieu chlorhydrique (ce qui aurait un grand intérêt pratique), nous avons répété les déterminations de R_F avec un échantillon contenant un peu de $BaCl_2$ (employé comme entraîneur dans l'obtention de AcX). Nous indiquerons ensuite les valeur obtenues et dans lesquelles nous voyons une diminution due probablement à un entraînement du Ra par le précipité de baryum.

HCl	1*N*	2*N*	4*N*	6*N*	8*N*	10*N*	12*N*
R_F	0	0	0.08	0.10	0.01	0.01	0

Il est possible qu'en utilisant un procédé de chromatographie descendante dans la zone 4 à 8*N*, on obtienne une séparation satisfaisante.

A_6 — La séparation de tous les éléments de cette colonne (excepté Ra) peut être faite depuis 8*N* jusqu'à 12*N*. Nous avons fait un essai avec un mélange des 5 éléments, en utilisant HCl 12*N*, et nous avons obtenu un beau chromatogramme avec les cinq taches totalement séparées.

Bibliographie p. 569

GROUPE III

A — Sc, Y, La, Ac (Fig. 5)

ions/[HCl]	1N	2N	4N	6N	8N	10N	12N	Révél.
Sc^{+3}	0.02 ± 0.02	0.04 ± 0.03	0.18 ± 0.04	0.40 ± 0.04	0.35 ± 0.04	0.31 ± 0.04	0.30 ± 0.05	(4)
Y^{+3}	0.01 ± 0.02	0.03 ± 0.02	0.17 ± 0.03	0.37 ± 0.03	0.31 ± 0.03	0.24 ± 0.03	0.20 ± 0.03	(4)
La^{+3}	0.01 ± 0.02	0.02 ± 0.02	0.15 ± 0.03	0.32 ± 0.02	0.26 ± 0.02	0.20 ± 0.02	0.17 ± 0.03	(4)
Ac^{+3} (^{228}Ac)	0.01	0.04	0.17	0.33	0.27	0.21	0.17	(2)
B — B, Al, Ga, In, Tl (Fig. 6)								
$BO_3H_2^-$	0.57 ± 0.05	0.62 ± 0.05	0.76 ± 0.06	0.76 ± 0.06	0.75 ± 0.05	0.67 ± 0.05	0.60 ± 0.06	(14)
Al^{+3}	0.01 ± 0.03	0.04 ± 0.03	0.21 ± 0.05	0.41 ± 0.07	0.38 ± 0.07	0.34 ± 0.06	0.27 ± 0.06	(7)
Ga^{+3}	0.21 ± 0.02	0.34 ± 0.02	0.76 ± 0.02	0.99 ± 0.02	1.00 ± 0.02	1.00 ± 0.02	0.91 ± 0.04	(7)
In^{+3}	0.24 ± 0.08	0.28 ± 0.08	0.45 ± 0.07	0.57 ± 0.08	0.55 ± 0.07	0.49 ± 0.06	0.45 ± 0.07	(7)
Tl^{+3}	0.80 ± 0.06	0.94 ± 0.04	0.99 ± 0.01	0.98 ± 0.02	0.98 ± 0.02	0.96 ± 0.02	0.95 ± 0.02	(15)

Observation. Comme B ne donne pas de cation, nous avons essayé une solution de $Na_2B_4O_7$ et une autre de H_3BO_3 (solutions saturées dans HCl 1*N*). Les valeurs présentées sont les moyennes des valeurs obtenues pour chaque solution lesquelles, d'ailleurs, ne sont pas très différentes.

LANTHANIDES — La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu (Fig. 7 et 8)

ions/[HCl]	1N	2N	4N	6N	8N	10N	12N	Révél.
La^{+3}	0.01	0.02	0.15	0.32	0.26	0.20	0.17	(4)
Ce^{+3}	0.01	0.02	0.17	0.33	0.27	0.22	0.17	(4)
Pr^{+3}	0.01	0.02	0.17	0.29	0.28	0.20	0.15	(4)
Nd^{+3}	0.01	0.02	0.17	0.31	0.28	0.20	0.16	(4)
Pm^{+3}	0.01	0.02	0.18	0.35	0.27	0.19	0.15	(2)
Sm^{+3}	0.01	0.02	0.17	0.31	0.26	0.21	0.16	(4)
Eu^{+3}	0.01	0.02	0.15	0.30	0.27	0.23	0.18	(4)
Gd^{+3}	0.01	0.03	0.19	0.34	0.30	0.24	0.19	(4)
Tb^{+3}	0.01	0.03	0.19	0.36	0.34	0.24	0.20	(4)
Dy^{+3}	0.01	0.02	0.20	0.37	0.34	0.25	0.20	(4)
Ho^{+3}	0.01	0.02	0.19	0.35	0.34	0.25	0.20	(4)
Er^{+3}	0.01	0.02	0.19	0.36	0.35	0.27	0.19	(4)
Tm^{+3}	0.01	0.01	0.18	0.37	0.34	0.26	0.18	(4)
Yb^{+3}	0.01	0.02	0.20	0.36	0.32	0.23	0.16	(4)
Lu^{+3}	0.01	0.02	0.19	0.37	0.31	0.23	0.16	(4)

Observation. Les chiffres présentés sont la moyenne de deux ou trois déterminations pour chaque élément, à l'exception de Pm, avec lequel nous avons fait une seule détermination pour chaque solution.

B_1 — La séparation de Zn d'avec Cd est difficile par chromatographie ascendante. Les deux meilleures zones sont 1*N* et 8-10*N*.

B_2 — La séparation du *mercure* des deux autres éléments peut s'effectuer facilement dans la zone 1*N*, et encore convenablement à 2*N*.

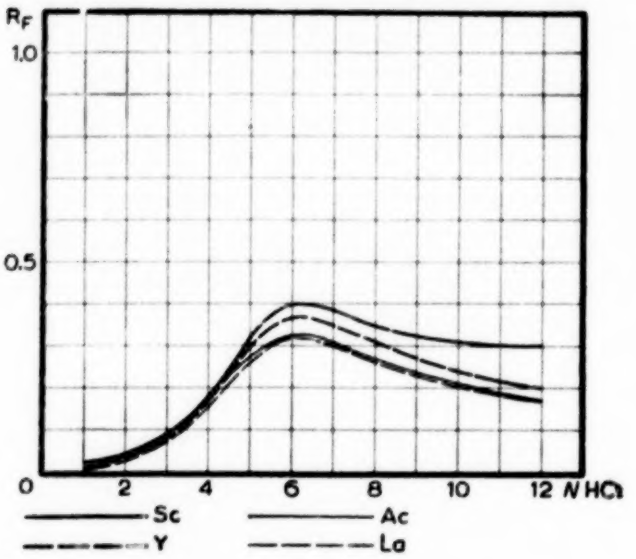

Fig. 5. Groupe III-A.

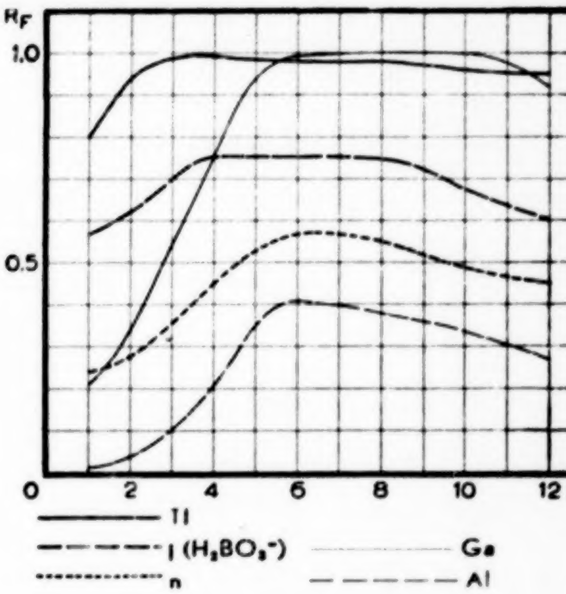

Fig. 6. Groupe III-B.

Observations sur les résultats (Groupe III)

A_1 — Le scandium peut être séparé de tous les autres depuis 6*N*, mais particulièrement bien dans la zone 10 à 12*N*.

A_2 — Nous ne croyons pas possible la séparation complète de Ac d'avec Y et La. Il faudrait, pour trouver une possibilité, étudier plus à fond la zone 12*N*, où la différence des R_F est la plus grande.

B_1 — La séparation des borates de tous les autres éléments du groupe est possible dans toutes les zones sauf à 4*N* où la courbe de Ga se croise avec la courbe des borates.

B_2 — Les valeurs de R_F de Ga montent brusquement et il y a seulement une zone dans laquelle la séparation de tous les éléments est possible — à 3*N*. D'ailleurs cette zone avait déjà été choisie dans un travail antérieur[1] pour effectuer la séparation de Ga, In, Ge et Be.

B_3 — L'*indium*, contrairement à Ga, donne des taches allongées dans toutes les zones. Il est possible d'effectuer la séparation de cet élément de tous les autres à partir de 3*N*.

B_4 — Le *thallium* commence par présenter des taches très allongées à 1 et 2*N*, mais à partir de 4*N* la tache devient ronde et aplatie. Les zones de séparation du Tl de tous les autres éléments du groupe sont de 1 à 4*N*. Au delà de cette zone il y a coïncidence avec les taches de gallium.

Observations sur les résultats (Lanthanides)

1 — Dans la Fig. 7 nous présentons la zone comprise entre les maxima et minima obtenus pour chaque élément. Dans la Fig. 8 on indique, pour chaque éluant étudié, les R_F obtenus avec toutes les lanthanides (plus le La), en traçant les courbes respectives de variation.

2 — La configuration de toutes les courbes est semblable, avec une accentuation des maxima et minima jusqu'à 8*N*, suivie d'un adoucissement jusqu'à 12*N*.

3 — Les courbes se présentent en général avec deux maxima (les zones centrales des terres rares légères et des terres rares lourdes) et trois minima (l'un pour La, l'autre dans la zone Pm-Eu et un autre pour Lu).

4 — Bien qu'on ne puisse pas l'affirmer d'une manière définitive, il semble que les maxima et minima se déplacent légèrement vers la gauche à mesure qu'augmente la concentration de l'acide.

5 — Avec le butanol HCl 8*N* la séparation du groupe La-Eu du groupe Tb-Tm, doit être possible.

6 — Nous avons l'intention d'exploiter les possibilités de séparation par chromatographie descendante avec les mélanges 8 et 10*N*, puisque les résultats obtenus sont intéressants.

7 — Il convient de noter la ressemblance entre la configuration générale de ces courbes et la courbe des volumes atomiques, laquelle semble être d'inverse de la première, c'est-à-dire, les minima de la courbe des R_F coïncident, approximativement, avec les maxima des volumes atomiques (La, Eu, Yb).

Bibliographie p. 569

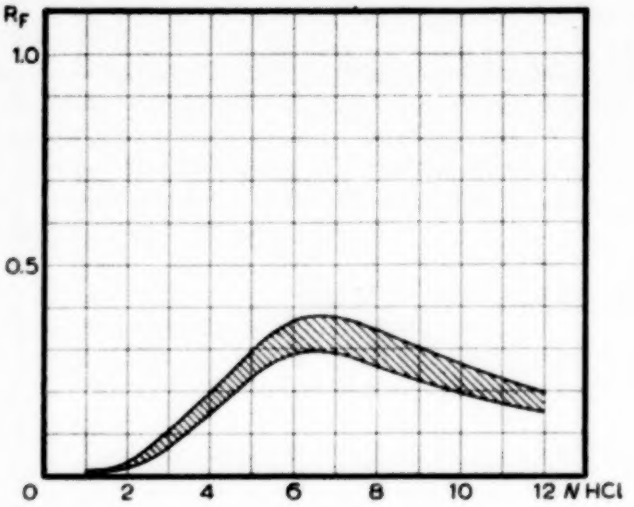

Fig. 7. Lanthanides.

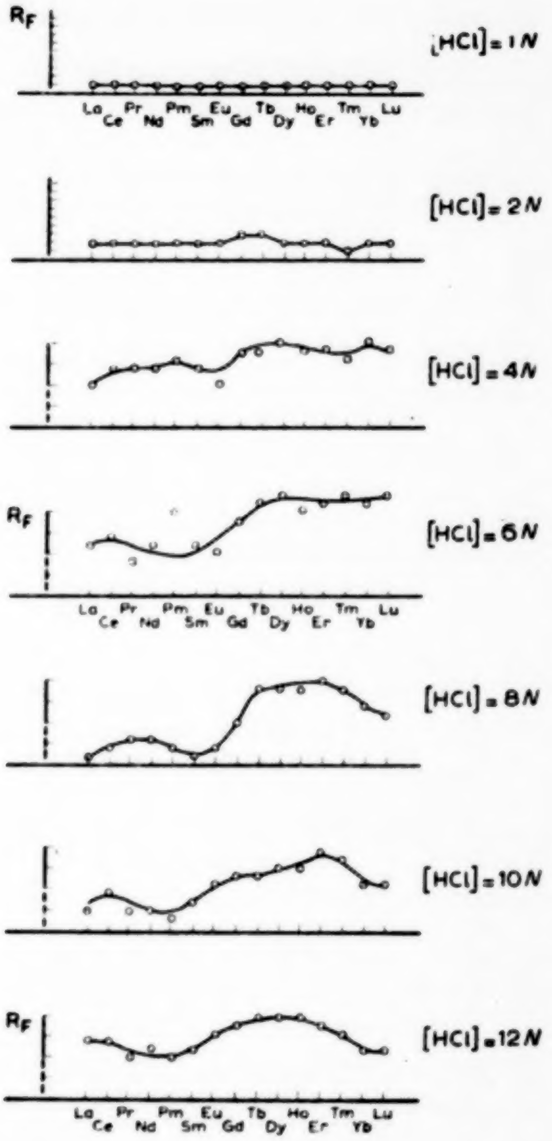

Fig. 8. Lanthanides.

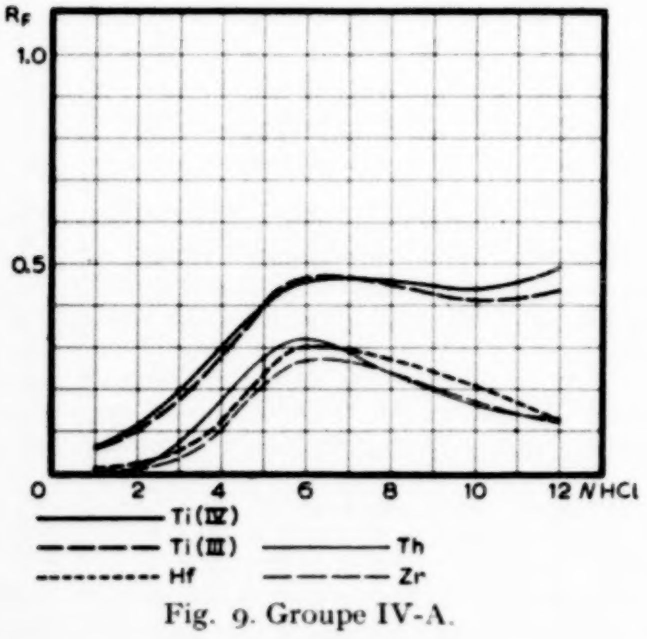

Fig. 9. Groupe IV-A.

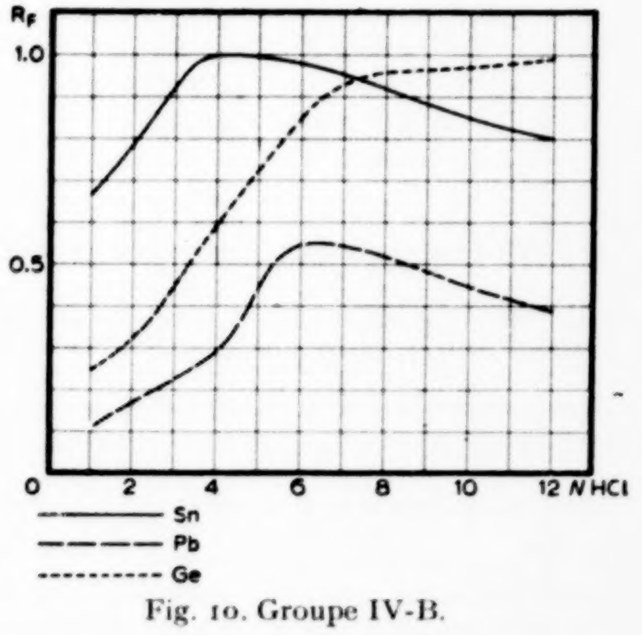

Fig. 10. Groupe IV-B.

Observations sur les résultats (Groupe IV)

A_1 — On ne note presque pas de différence dans le comportement de Ti(III) et de Ti(IV). Il semble seulement qu'avec les solutions plus acides, il y a une légère augmentation des R_F de Ti(IV) par rapport aux R_F de Ti(III).

A_2 — Il est possible d'obtenir une séparation complète de Ti des autres éléments du groupe à partir de $4N$, la meilleure séparation étant obtenue à $12N$.

Bibliographie p. 569

GROUPE IV

A — Ti, Zr, Hf, Th (Fig. 9)

ions/*[HCl]*	*1N*	*2N*	*4N*	*6N*	*8N*	*10N*	*12N*	*Révél.*
Ti^{+3}	0.06 ± 0.03	0.10 ± 0.02	0.28 ± 0.04	0.47 ± 0.03	0.45 ± 0.04	0.41 ± 0.04	0.44 ± 0.07	(6)
Ti^{+4}	0.06 ± 0.03	0.11 ± 0.03	0.30 ± 0.04	0.46 ± 0.04	0.46 ± 0.04	0.44 ± 0.04	0.49 ± 0.05	(6)
ZrO^{+2}	0 ± 0.02	0.01 ± 0.03	0.10 ± 0.04	0.27 ± 0.07	0.24 ± 0.05	0.17 ± 0.05	0.12 ± 0.07	(7)
Hf^{+4}	0.01 ± 0.02	0.02 ± 0.03	0.12 ± 0.04	0.30 ± 0.06	0.27 ± 0.05	0.21 ± 0.04	0.12 ± 0.05	(7)
Th^{+4}	0 ± 0.01	0.01 ± 0.01	0.17 ± 0.02	0.32 ± 0.02	0.24 ± 0.02	0.16 ± 0.02	0.13 ± 0.02	(4)
				B — Ge, Sn, Pb (Fig. 10)				
Ge^{+4}	0.25 ± 0.05	0.32 ± 0.05	0.60 ± 0.07	0.85 ± 0.08	0.96 ± 0.04	0.97 ± 0.03	0.99 ± 0.02	(16)
Sn^{+2} et Sn^{+4}	0.67 ± 0.02	0.79 ± 0.02	1.00 ± 0.01	0.98 ± 0.03	0.92 ± 0.04	0.85 ± 0.03	0.80 ± 0.03	(4)
Pb^{+2}	0.11 ± 0.02	0.17 ± 0.02	0.39 ± 0.03	0.55 ± 0.02	0.52 ± 0.03	0.45 ± 0.04	0.39 ± 0.04	(13)

GROUPE V

A — V, Nb, Ta, Pa (Fig. 11)

ions/*[HCl]*	*1N*	*2N*	*4N*	*6N*	*8N*	*10N*	*12N*	*Révél.*
VO^{+2}	0.11 ± 0.08	0.14 ± 0.09	0.26 ± 0.10	0.48 ± 0.09	0.43 ± 0.09	0.36 ± 0.09	0.31 ± 0.07	(4)
Nb^{+5}	0	0	0	0	0	0	0	(6)
Ta^{+5}	0	0	0	0	0	0	0	(4)
Pa^{+5}(^{233}Pa)	0	0.01	0.02	0.02	0.03	0.03	0.02	(2)
				B — N, P, As, Sb, Bi (Fig. 12)				
NH_4^+	0.08 ± 0.04	0.11 ± 0.04	0.28 ± 0.05	0.52 ± 0.05	0.51 ± 0.06	0.42 ± 0.05	0.38 ± 0.06	(17)
$H_2PO_4^-$	0.55 ± 0.05	0.66 ± 0.04	0.91 ± 0.04	0.93 ± 0.04	0.90 ± 0.05	0.78 ± 0.04	0.77 ± 0.04	(18)
As^{+3}	0.52 ± 0.06	0.57 ± 0.06	0.83 ± 0.05	0.96 ± 0.04	0.92 ± 0.03	0.84 ± 0.03	0.77 ± 0.04	(19)
As^{+5}	0.62 ± 0.04	0.71 ± 0.05	0.92 ± 0.03	0.97 ± 0.03	0.92 ± 0.03	0.86 ± 0.03	0.77 ± 0.04	(19)
Sb^{+3}	0.65 ± 0.03 (queue jusqu'à 0.54)	0.76 ± 0.02 (queue jusqu'à 0.67)	0.99 ± 0.01	0.95 ± 0.02	0.83 ± 0.02	0.77 ± 0.03	0.73 ± 0.04	(19)
Bi^{+3}	0.56 ± 0.04	0.61 ± 0.05	0.73 ± 0.07	0.79 ± 0.04	0.68 ± 0.05	0.58 ± 0.05	0.49 ± 0.05	(13)

Observations. Pour Nb et Ta nous sommes partis des oxydes, lesquels ont été fondus en creuset de quartz avec $K_2S_2O_7$. Après dissolution de la masse fondue dans H_2SO_4 concentré, la solution a été diluée et immédiatement après, precipitée par l'ammoniaque. Le précipité a été filtré, lavé et digéré avec HCl concentré. Après dilution on filtre et le filtrat est concentré par évaporation. En partie parce qu'il y a décomposition des nitrates par HCl, en partie parce qu'il est difficile de les détecter sur le papier, nous n'avons pas réussi à faire l'étude de ces anions. Cependant, nous avons étudié le cation NH_4^+.

A_3 — Le zirconium présente en général des taches allongées dues probablement à une faible solubilité ou hydrolyse du $ZrOCl_2$.

A_4 — L'hafnium a un comportement identique à celui de Zr. Il nous semble possible de séparer Hf de Zr en employant comme éluant du butanol + HCl 10*N*, avec une petite quantité de HCl, et en employant une technique descendante.

A_5 — Le thorium qui a une courbe absolument identique à celles des terres rares, se superpose en beaucoup de points à celles de Zr et de Hf. Nous ne croyons pas possible la séparation de cet élément des deux précédents.

B_1 — Les taches de germanium sont très élargies dans les zones de 1 à 6*N*. Après cette zone les taches sont sur le front du solvant.

La séparation de Ge-Sn peut être effectuée dans toutes les zones sauf entre 6 et 10*N*. Elle est particulièrement bonne entre 1 et 4*N*. La séparation Ge-Pb peut se faire dans toutes les zones étudiées.

B_2 — Le *plomb* présente des taches qui s'allongent à mesure qu'on emploie des solutions plus concentrées en acide, ce qui est peut-être dû à une plus grande insolubilité dans ces zones.

Le changement brusque qu'on note dans la courbe entre 4 et 6*N*, doit être dû, probablement, à la formation d'un complexe plus chloré ($PbCl^+$, ou même $PbCl_2$, ou $PbCl_3^-$, . . .) lequel présente un R_F plus grand.

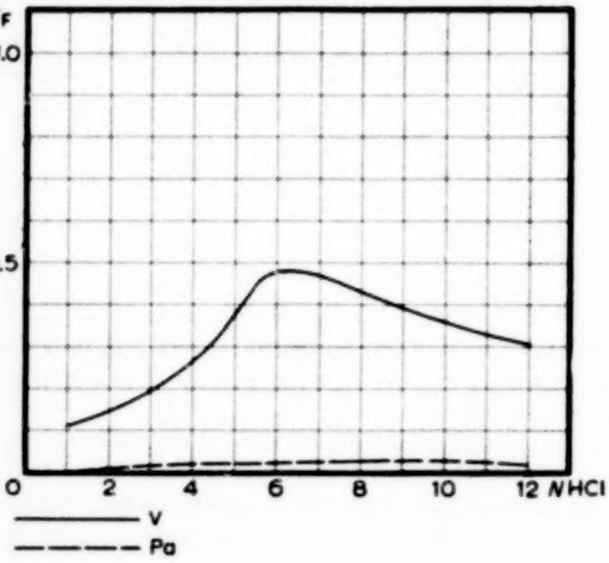

Fig. 11. Groupe V-A.

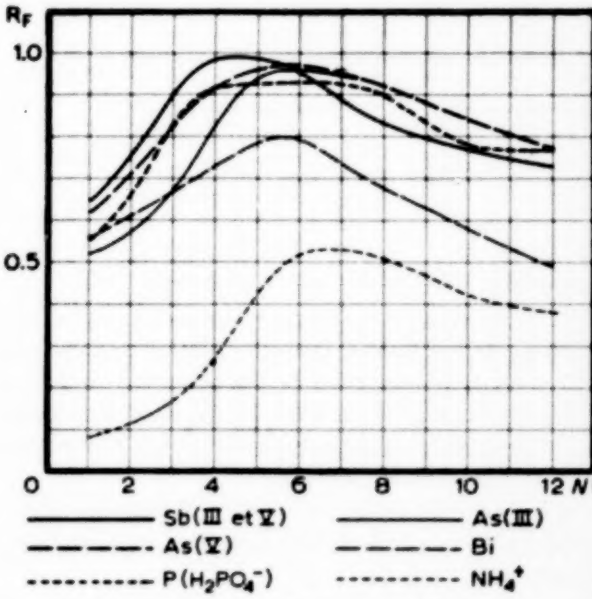

Fig. 12. Groupe V-B.

Observations sur les résultats (Groupe V)

A_1 — Les taches obtenues avec le vanadium sont toutes très allongées, cependant la longueur de la tache diminue au fur et à mesure que l'acidité croit.

En utilisant des solutions diluées de V, on peut noter parfaitement que, avec les acides 1 et 2*N*, il y a trois taches successives, lesquelles n'étant pas totalement séparées les unes des autres, donnent l'aspect d'une tache unique et allongée.

A_2 — Avec les solutions 1 et 2*N*, la tache du Nb présente une légère tendance à se mouvoir, tandis qu'avec les acides plus concentrés on ne note aucun déplacement. Cela doit être dû à une plus grande insolubilité dans l'acide concentré.

A_3 — Le protactinium se déplace très peu, et laisse toujours une comète, la plus grande partie de l'élément restant sur la tache originelle.

B_1 — L'*ammonium* peut se séparer très bien de tous les autres ions du groupe. Sa courbe est si semblable à celles des alcalins (elle est presque superposable à celle du lithium), qu'on ne peut pas le séparer de ces éléments.

B_2 — Pour les *phosphates* les résultats présentés sont la moyenne des trois solutions essayées, lesquelles d'ailleurs donnaient des valeurs pratiquement égales (avec un maximum de différence entre eux 0.02 de R_F).

Les taches qui au début sont un peu allongées, deviennent de plus en plus régulières.

Il n'est pas possible de séparer ces ions des autres ions du même groupe à l'exception du Bi qui peut se séparer à partir de 4*N*.

Bibliographie p. 569

B_3 — L'*arsenic(III)* se déplace moins que l'arsenic (V). Les taches qui au début sont allongées deviennent de plus en plus aplaties.

B_4 — Les taches de Sb marchent avec le front aqueux, laissant une longue queue jusqu'à 2*N*, ce qui est dû, probablement, à l'hydrolyse du sel en milieu faiblement acide.

B_5 — Le *bismuth* a une courbe assez différente de celles des autres éléments du groupe, pour qu'il soit possible de le séparer dans les zones entre 6 et 10*N*, et en particulier dans cette dernière.

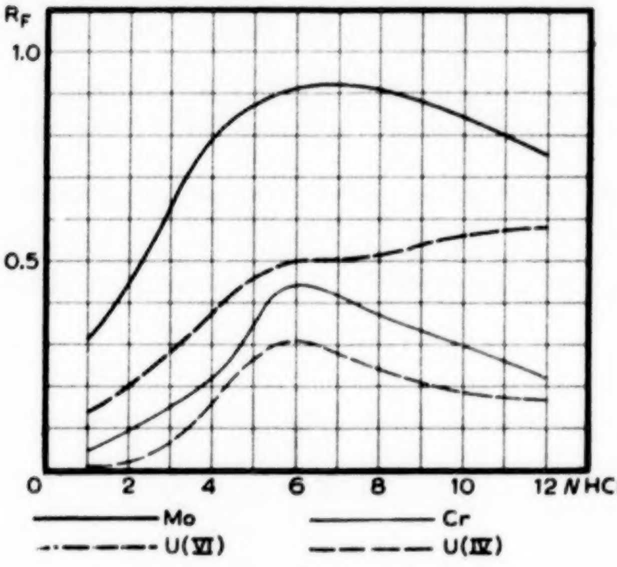

Fig. 13. Groupe VI-A.

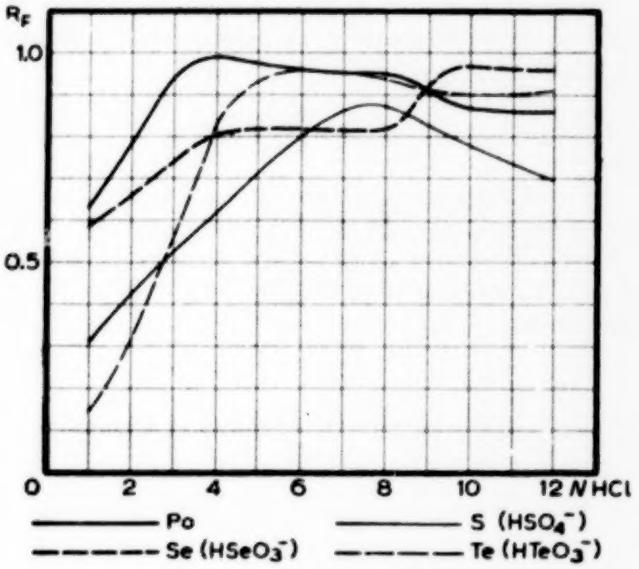

Fig. 14. Groupe VI-B.

Observations sur les résultats (Groupe VI)

A_1 — Le chrome qui présente une courbe très semblable à celle de V du groupe précédent, peut se séparer facilement des éléments de ce groupe à partir de 6*N*, une fois que l'uranium soit à la valence 6.

A_2 — Avec le molybdène on observe un grand allongement avec les solutions 1 et 2*N*, ce que nous supposons être dû à la formation de complexes plus chlorés de Mo.

A_3 — Quant à l'uranium, on voit qu'une séparation complète de U(VI) de U(IV) est possible, quelle que soit la solution utilisée.

Il est intéressant de noter que la courbe de U(VI) est totalement modifiée à partir de 6*N*, relativement à la forme habituelle des autres courbes, ce qui suppose la formation d'un autre complexe, à cette acidité.

Il convient aussi de noter que la courbe de U(IV) est absolument identique à celles de Th et des terres rares.

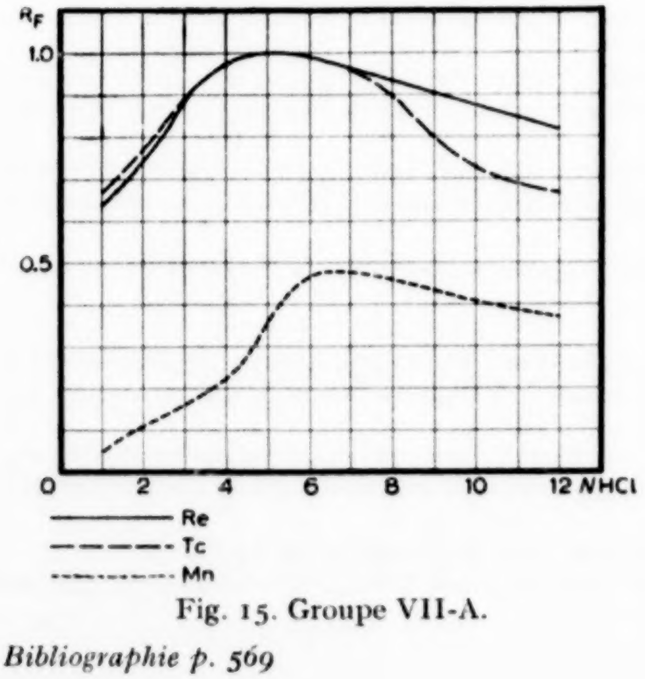

Fig. 15. Groupe VII-A.

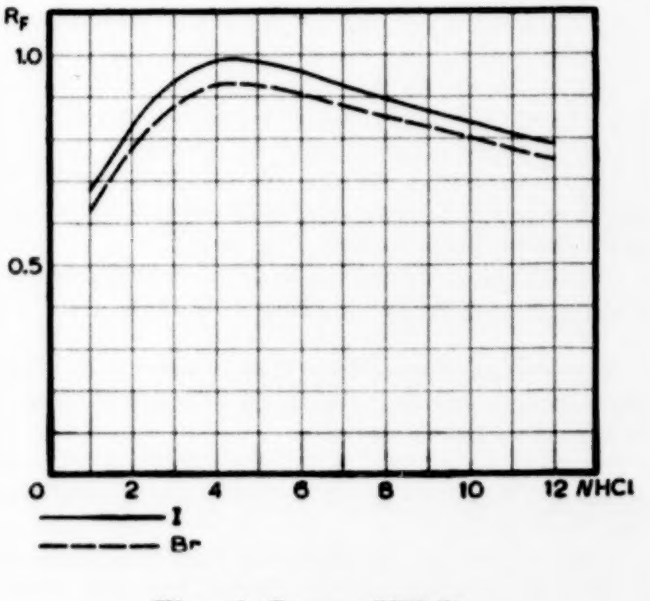

Fig. 16. Groupe VII-B.

Bibliographie p. 569

GROUPE VI

A — Cr, Mo, W, U (Fig. 13)

ions/[HCl]	1N	2N	4N	6N	8N	10N	12N	Révél.
Cr^{+3}	0.05 ± 0.04	0.09 ± 0.04	0.22 ± 0.05	0.44 ± 0.04	0.37 ± 0.04	0.30 ± 0.05	0.22 ± 0.05	(22)
Mo^{+6}	0.31 ± 0.10	0.45 ± 0.10	0.79 ± 0.08	0.91 ± 0.05	0.91 ± 0.04	0.84 ± 0.05	0.75 ± 0.06	(8)
W^{+6}	0	0	0	0	0	0	0	(8)
UO_2^{+2}	0.14 ± 0.04	0.20 ± 0.04	0.37 ± 0.05	0.50 ± 0.06	0.51 ± 0.06	0.56 ± 0.06	0.58 ± 0.06	(23)
UO^{+2}	0.01 ± 0.02	0.02 ± 0.02	0.16 ± 0.03	0.31 ± 0.04	0.24 ± 0.04	0.19 ± 0.03	0.17 ± 0.03	(23)

B — S, Se, Te, Po (Fig. 14)

ions/[HCl]	1N	2N	4N	6N	8N	10N	12N	Révél.
HSO_4^-	0.31	0.44	0.62	0.80	0.87	0.78	0.70	(a)
$HSeO_3^-$	0.59 ± 0.04	0.66 ± 0.04	0.81 ± 0.04	0.82 ± 0.05	0.82 ± 0.03	0.97 ± 0.03	0.96 ± 0.04	(11)
$HTeO_3^-$	0.15 ± 0.05	0.32 ± 0.05	0.84 ± 0.03	0.96 ± 0.04	0.95 ± 0.05	0.90 ± 0.03	0.91 ± 0.04	(11)
Po^{+4}(^{210}Po)	0.63	0.79	0.99	0.96	0.95	0.87	0.86	(20)

(a) Chaque chromatogramme a été coupé en morceaux de 1 cm de largeur, lesquels ont été traités séparément dans l'eau, les solutions sont précipitées par $BaCl_2$. On peut ainsi déceler la place où se trouve la tache de HSO_4^-.

GROUPE VII

A — Mn, Tc, Re (Fig. 15)

ions/[HCl]	1N	2N	4N	6N	8N	10N	12N	Révél.
Mn^{+2}	0.05 ± 0.03	0.11 ± 0.03	0.22 ± 0.07	0.47 ± 0.07	0.46 ± 0.07	0.41 ± 0.06	0.37 ± 0.07	(4)
TcO_4^-(^{99}Tc)	0.67	0.77	0.98	0.99	0.90	0.73	0.67	(2)
ReO_4^-(^{186}Re)	0.64 ± 0.02	0.74 ± 0.03	0.98 ± 0.02	0.99 ± 0.02	0.93 ± 0.05	0.88 ± 0.05	0.82 ± 0.05	(2) (8)

B — Br, I (Fig. 16)

ions/[HCl]	1N	2N	4N	6N	8N	10N	12N	Révél.
Br^-	0.63 ± 0.02	0.78 ± 0.02	0.93 ± 0.04	0.91 ± 0.04	0.85 ± 0.04	0.81 ± 0.04	0.75 ± 0.05	(21)
I^-	0.68 ± 0.04	0.83 ± 0.05	0.99 ± 0.01	0.96 ± 0.02	0.89 ± 0.02	0.84 ± 0.02	0.79 ± 0.03	(22)

B_1 — Le *sélénite* a une zone optimum de séparation du tellure à 1*N*, bien qu'on puisse aussi les séparer aisément dans les zones 2,6 et 8*N*.

On doit noter la forme curieuse présentée par la courbe de Se à partir de 8*N*, laquelle doit être due à la formation d'une nouvelle espèce ionique au delà de cette concentration d'acide.

B_2 — Seul le *tellurite* dans les zones 1 et 2*N* peut être séparé complètement de tous les autres ions du groupe. Dans ces zones les taches sont allongées "vers l'avant".

Il est probable que l'espèce ionique finale soit du même type de celle du Se.

B_3 — Le *polonium* marche sensiblement avec le front aqueux. La seule zone où une séparation totale des autres éléments du groupe est possible est celle qui est comprise entre 2 et 3*N*.

B_4 — A 2*N* une séparation complète de tous les éléments du groupe peut être effectuée.

Observations sur les résultats (Groupe VII)

A_1 — La chromatographie du Tc ne semble avoir été étudiée que par M. Lederer qui a utilisé comme solvant du butanol + HCl 1*N*.

La courbe que nous venons de tracer nous permet de vérifier que Tc se comporte comme Re jusqu'à 6*N*, puis s'en écarte progressivement pour présenter à 12*N* une différence de 0.12 dans les valeurs de R_F, ce qui permet une belle séparation des deux éléments.

Ce résultat est intéressant, étant donné que les méthodes de séparation des deux éléments ne sont pas très nombreuses.

A_2 — La courbe obtenue pour le *rhénium* se montre très semblable à celle du molybdène, avec toutefois des valeurs de R_F toujours supérieures. Dans la zone 1-4*N* nous pouvons obtenir des séparations complètes, ce qui peut avoir un très grand intérêt pratique dans le dosage de Re dans les molybdénites.

B_1 — Une séparation partielle des deux éléments sera peut-être possible de 4 à 6*N*.

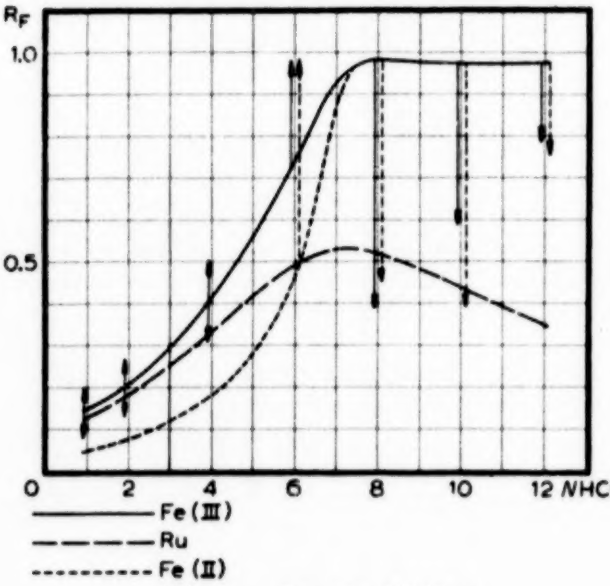

Fig. 17. Groupe VIII-A.

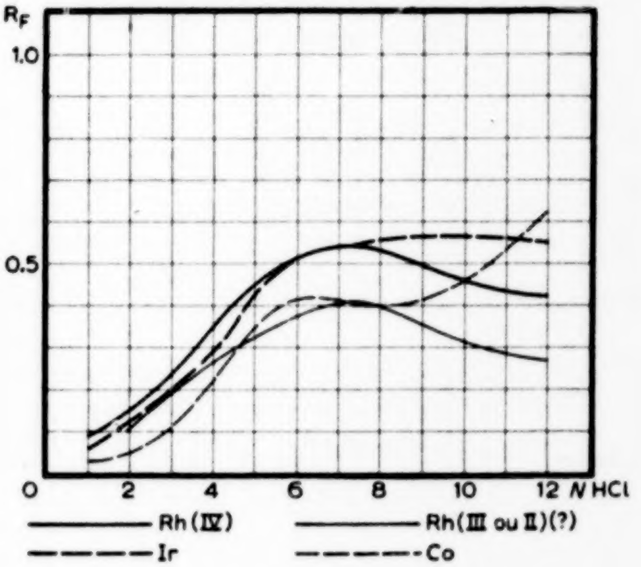

Fig. 18. Groupe VIII-B.

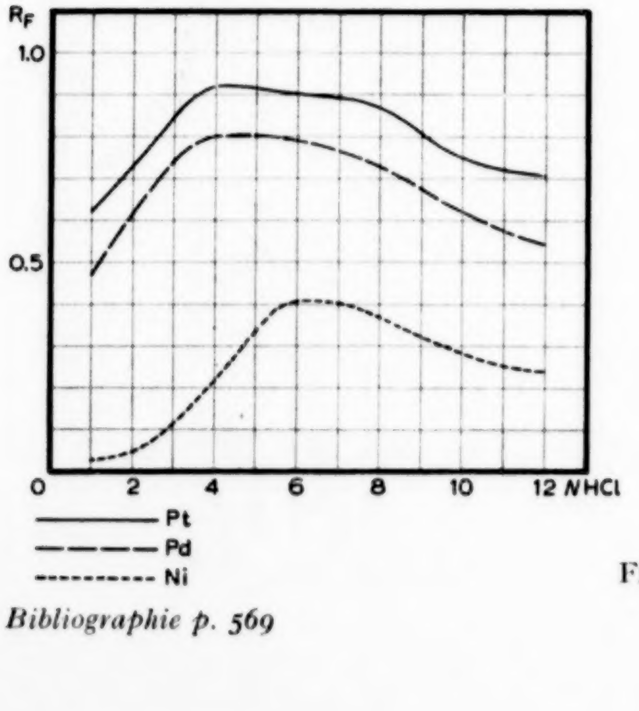

Fig. 19. Groupe VIII-C.

Bibliographie p. 569

GROUPE VIII

A — Fe, Ru (Fig. 17)

ions/[HCl]	*1N*	*2N*	*4N*	*6N*	*8N*	*10N*	*12N*	*Révél.*
Fe^{+2}	0.05 ± 0.05	0.07 ± 0.05	0.18 ± 0.08	0.45 ± 0.07 0.98 ± 0.02	0.46 ± 0.09 0.98 ± 0.02	0.97 ± 0.03 (queue jusqu'à 0.40)	0.97 ± 0.03 (queue jusqu'à 0.76)	(4)
Fe^{+3}	0.09 ± 0.04 0.20 ± 0.03	0.14 ± 0.03 0.27 ± 0.06	0.31 ± 0.04 0.51 ± 0.10	0.49 ± 0.05 0.98 ± 0.02	0.39 ± 0.06 0.98 ± 0.02	0.97 ± 0.03 (queue jusqu'à 0.59)	0.97 ± 0.03 (queue jusqu'à 0.79)	(4)
Ru^{+4}	0.13 ± 0.03 et queue	0.18 ± 0.03 et queue	0.33 ± 0.03	0.49 ± 0.03	0.52 ± 0.03	0.44 ± 0.03	0.35 ± 0.03	(10)
B — Co, Rh, Ir (Fig. 18)								
Co^{+2}	0.03 ± 0.03	0.05 ± 0.04	0.22 ± 0.05	0.42 ± 0.07	0.40 ± 0.07	0.46 ± 0.07	0.63 ± 0.11	(4)
Rh^{+4}	0.09 ± 0.03 (queue jusqu'à 0)	0.15 ± 0.03 0.11 ± 0.03 0.05 ± 0.02	0.35 ± 0.04 0.27 ± 0.03 0.19 ± 0.03	0.52 ± 0.04 0.38 ± 0.04	0.53 ± 0.03 0.40 ± 0.02	0.46 ± 0.03 0.31 ± 0.03	0.42 ± 0.03 0.27 ± 0.02	(11)
Ir^{+4}	0.06 ± 0.02	0.12 ± 0.03	0.39 ± 0.04	0.51 ± 0.04	0.56 ± 0.04	0.57 ± 0.04	0.55 ± 0.04	(12)
C — Ni, Pd, Pt (Fig. 19)								
Ni^{+2}	0.03 ± 0.03	0.05 ± 0.03	0.22 ± 0.05	0.41 ± 0.07	0.37 ± 0.07	0.28 ± 0.06	0.24 ± 0.05	(4)
Pd^{+4}	0.47 ± 0.04	0.62 ± 0.04	0.80 ± 0.03	0.79 ± 0.04	0.73 ± 0.04	0.62 ± 0.03	0.54 ± 0.05	(11)
Pt^{+4}	0.62 ± 0.04	0.73 ± 0.04	0.92 ± 0.03	0.90 ± 0.05	0.87 ± 0.05	0.75 ± 0.06	0.71 ± 0.08 (queue jusqu'à 0.51)	(11)

Observation. Dans tous les cas où il y a deux taches, on a noté toujours une tache de liaison plus claire et plus étroite. Les valeurs soulignées sont celles des taches bien marquées.

Observations sur les résultats

A_1 — Le Fe(II) se comporte différemment du Fe(III) jusqu'à 8*N*, présentant à partir de là la même courbe. Peut-être cela est-il dû à l'oxydation de Fe(II) en milieu fortement chlorhydrique.

A_2 — Le Fe(III) a des valeurs de R_F supérieures à celles de Fe(II) jusqu'à 8*N*, ce qui est probablement dû à une plus grande solubilité du sel ferrique.

L'obtention de taches doubles est peut-être due à l'existence simultanée de deux sortes d'ions du fer.

A_3 — Le Ru présente des comètes avec les solutions 1 et 2*N*, ce qui ne se vérifie pas aisément avec les autres solutions.

Seule la séparation Ru-Fe sera possible dans la zone 12*N*.

B_1 — Le Rh présente deux, et même trois taches, en solutions diluées. Avec la solution 1*N*, on note une tache bien marquée et une queue jusqu'à 0. Avec les solutions 2 et 4*N* les trois taches sont bien marquées. Avec les solutions 6 à 12*N*, on observe seulement deux taches bien séparées l'une de l'autre.

Dans tous les cas, la première tache, c'est-à-dire, celle de plus grand R_F, est la plus foncée, tandis que la troisième, quand elle existe, est toujours la plus faible.

B_2 — En comparant les courbes du rhodium et du ruthénium, on conclut que la séparation de ces deux éléments est impossible dans les conditions de nos expériences.

B_3 — L'iridium peut être séparé du rhodium, et aussi du ruthénium, seulement dans les zones 9 à 12*N*.

C_1 — Le *nickel* présente des taches identiques par la forme et les R_F, à celles du cobalt. Mais, contrairement au Co, les taches deviennent moins longues à mesure que l'acidité croît. Cependant dans la zone 10-12*N* le R_F du Co croît brusquement, ce qui permet une belle séparation des deux éléments dans cette région.

C_2 — Le *palladium* présente des taches régulières dans toutes les zones, une bonne séparation du platine étant toujours possible, sauf dans la zone 12*N* où le Pt donne une queue très étendue.

Cet élément peut se séparer de Rh et Ru dans toutes les zones étudiées. La séparation du Ir convient seulement dans la zone 1 à 8*N*.

C_3 — Les taches de platine s'allongent avec l'acidité de la solution de telle façon qu'à 12*N* la queue s'étend par 0.20 de R_F.

La séparation de Rh et Ru est possible dans toutes les zones. La séparation de Ir convient dans la zone 1 à 10*N*.

CONCLUSIONS

Nous avons tracé sur chaque graphique les courbes de tous les éléments de chaque groupe du tableau périodique, dont nous avons déterminé *simultanément* les valeurs de R_F. L'examen de ces courbes nous a permis de déterminer les meilleures conditions de séparation des éléments du même groupe, et d'obtenir des séparations qui avaient été impossibles avec les éluants étudiés jusqu'ici.

Les conclusions sur U(IV) et sur les terres rares sont à signaler.

L'examen simultané des courbes peut nous donner des indications sur les séparations possibles entre éléments de groupes différents, mais nous devons nous rappeler toujours qu'il faut au moins une différence de 0.10 entre les valeurs des R_F, pour que la séparation soit raisonnable. Si la différence est plus petite, il peut arriver qu'on puisse parvenir à une séparation, mais il faudra essayer divers mélanges des éléments à séparer et tenter parfois la chromatographie descendante.

Nous avons signalé quelques séparations intéressantes entre éléments de groupes différents mais qui ont un grand intérêt analytique, tels que: nickel du cobalt, molybdène du rhénium, éléments de la famille du platine, etc. On pourrait en envisager beaucoup d'autres comme: Be-Al, Th-U, Sn-Sb, etc.

Nous avons signalé aussi beaucoup d'anomalies, observées dans les courbes; quelques hypothèses sont faites pour tenter une explication. Toutefois, seule une étude plus approfondie pourra éclaircir ces questions.

Beaucoup de séparations pas très nettes, mais qui deviendront peut-être possibles avec de légères variations de conditions ou de techniques, ont été indiquées.

Bibliographie p. 569

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RÉSUMÉ

On détermine les valeurs de R_F de 79 éléments en utilisant la chromatographie ascendante sur papier et comme éluants des mélanges 1 : 1 de *n*-butanol et d'acide chlorhydrique 1, 2, 4, 6, 8, 10 et 12*N* (les mélanges 1,2 et 4*N* donnent deux phases). On trace les courbes de variation du R_F de chaque élément avec la concentration de l'acide. On fait une étude critique des conditions les plus favorables pour séparer les éléments d'un même groupe, et, parfois, de groupes différents. On essaie d'expliquer certaines anomalies constatées.

SUMMARY

The R_F values of 79 elements have been determined by paper chromatography using ascending development. The eluants used were 1 : 1 mixtures of *n*-butanol and 1, 2, 4, 6, 8, 10 and 12*N* hydrochloric acid (the 1,2 and 4*N* mixtures give two phases). The curves of R_F variation of the elements versus the acid concentration have been plotted. A critical study has been made of the most favourable conditions for separating elements of the same group and, sometimes, of different groups. The author attempts to explain certain anomalies that have been found.

ZUSAMMENFASSUNG

Die R_F-Werte von 79 Elementen wurden papierchromatographisch (bei aufsteigender Entwicklung) bestimmt. Als Elutionsmittel wurden Gemische im Verhältnis 1 : 1 von *n*-Butanol und 1, 2, 4, 6, 8, 10- und 12-normaler Salzsäure verwendet (die Gemische mit 1,2- und 4-normaler Säure ergaben zwei Phasen). Für jedes Element wurde die Kurve der Variation von R_F in Funktion der Säurekonzentration gezeichnet. Eine kritische Untersuchung der günstigsten Bedingungen zur Trennung der Elemente einer selben Gruppe und, manchmal, von verschiedenen Gruppen, wurde ausgeführt. Der Verfasser versucht einige beobachtete Abweichungen zu erklären.

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A NEW SPECTROPHOTOMETRIC METHOD FOR THE DETERMINATION OF CALCIUM WITH THE DISODIUM SALT OF ETHYLENEDIAMINETETRAACETIC ACID

by

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INTRODUCTION

During a series of experiments on the development of a simple and efficient method for estimation of calcium content in sugarcane juices, which has been a problem in sugar technological laboratories, a new method of estimation of Ca^{+2} with the disodium salt of ethylenediaminetetraacetic acid (EDTA, versene) has been developed using the characteristic absorption of copper ammonium complex in the visible region; in this method, the copper ammonium complex has been used as an indicator.

EXPERIMENTAL PART

Reagents

Recrystallised calcium nitrate (Merck quality). The amount of calcium in the calcium nitrate solution was determined by the usual oxalate method.

Copper sulphate of B.D.H. AnalaR quality.

Disodium salt of ethylenediaminetetraacetic acid (versenate) of Merck quality. A 50 m*M* solution of this was prepared by dissolving 18.61 g in 1000 ml of twice distilled water.

Pure ammonia free from carbonate.

The spectrophotometer employed was a Unicam S.P.350 D.G. spectrophotometer; this had continuous variation of wavelength from $\lambda = 400$ to 700 mμ; and 1 cm light path.

Procedure

Aliquots of the standard solutions of Ca^{+2} and Cu^{+2} were pipetted out into calibrated 25 ml flasks. A calculated quantity of ammonia was then added; the final solution (25 ml) contained $2M$ NH_4OH. Increasing quantities of versenate were added and then the volume was made up to 25 ml with distilled water. A measured sample of these solutions was taken in the absorption cell and the absorbancy was measured on the spectrophotometer.

RESULTS

The results reported in this article were obtained with standard solutions of Ca^{+2} and Cu^{+2}.

Fig. 1 shows the absorption spectrum of the copper ammonium complex in the visible region, which reveals that a distinct absorption maximum at $\lambda = 630$ mμ is exhibited by the copper ammonium complex and further that the absorption at $\lambda = 630$ mμ obeys Beer's law with a value of 50 $mole^{-1}$ litre cm^{-1} for the corresponding constant.

A typical set of curves for the titration of calcium nitrate with the disodium salt of ethylenediaminetetraacetic acid is given in Fig. 2; in this, the scale on the Y-axis refers to the optical density or the colour of the copper ammonium complex which has been employed as the indicator. The indicator material was added usually in relatively small concentration; in the present method, however, the indicator has been used in a concentration comparable with that of the sample being determined. The curves in Fig. 2

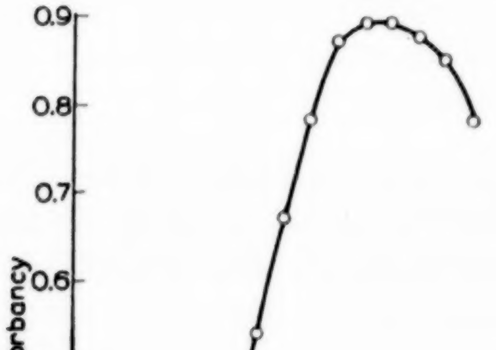

Fig. 1. Absorption spectrum of copper ammonium complex in the visible region. Concentration of Cu^{+2}: 20 m*M*; concentration of NH_4OH: 1.15*M*.

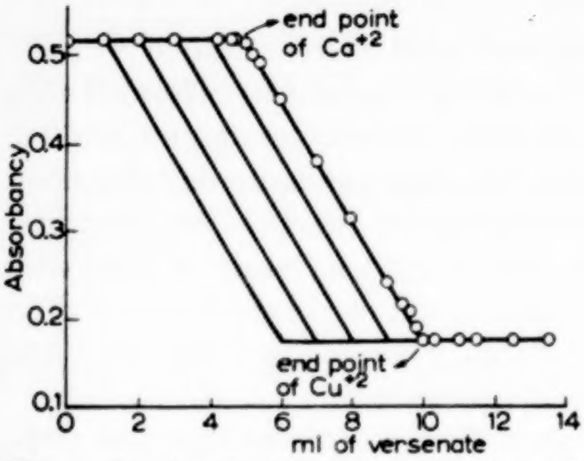

Fig. 2. Spectrophotometric end-points of Ca^{+2} and Cu^{+2} with versenate. λ: 630 mμ. Concentration of versenate: 50 m*M*; concentration of NH_4OH: 2.14*M*; concentration of Cu^{+2}: 10 m*M*; curve 1 refers to a concentration of 2; curve 2 to 4, curve 3 to 6, curve 4 to 8 and curve 5 to 10 m*M* of Ca^{+2}.

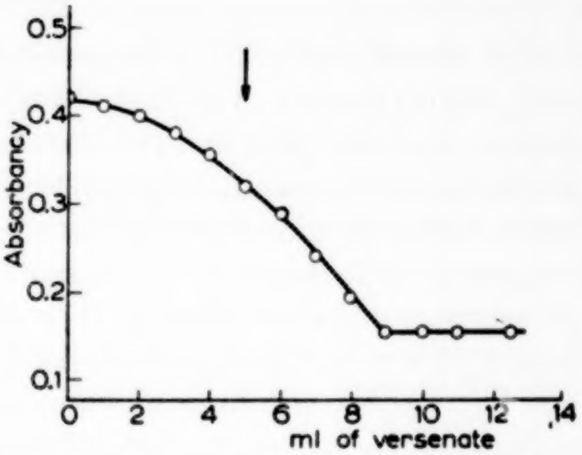

Fig. 3. Failure of the spectrophotometric titration of Ca^{+2} with versenate at low concentrations of of NH_4OH. λ: 630 mμ. Concentration of Ca^{+2}: 10 m*M*; concentration of Cu^{+2}: 8 m*M*; concentration of NH_4OH: 0.53*M*; concentration of versenate: 50 m*M*.

refer to a fixed concentration of Cu^{+2} (10 m*M*). Further, the curves are linear with no change in the optical density during the titration of Ca^{+2}, because neither calcium nor calcium versenate shows appreciable absorption at $\lambda = 630$ mμ. The end-points were very sharp under the experimental conditions of high concentrations of ammonia ($> 1.5M$). It has been observed that at low concentrations, however, the end-points were not well defined in the sense that the absorbancy decreased gradually with addition of versenate during the titration of Ca^{+2} (see Fig. 3).

TABLE I

ESTIMATION OF CALCIUM WITH EDTA

Experiment nr	*Indicator concn. (Cu^{+2}, mg)*	*Ca^{+2} taken mg*	*Ca^{+2} found mg*	*Error %*
1	62.4_2	59.8_9	59.6_2	0.45
2	,,	47.9_1	47.8_1	0.21
3	,,	35.9_3	36.5_9	1.86
4	,,	23.9_6	23.6_1	1.45
5	,,	11.9_8	11.8_1	1.42
6	49.9_4	59.8_9	59.0_3	1.43
7	,,	47.9_1	47.8_1	0.21
8	,,	35.9_3	36.0_1	0.22
9	,,	23.9_6	23.6_1	1.45
10	,,	11.9_8	11.8_1	1.42
11	37.4_6	59.8_9	59.6_2	0.45
12	,,	47.9_1	47.2_2	1.44
13	,,	35.9_3	36.0_1	0.22
14	,,	23.9_6	23.9_1	0.21
15	,,	11.9_8	11.8_1	1.42

The data in Table I show that the method can be employed satisfactorily over a wide range of concentrations of Ca^{+2} and the error involved in the procedure was less than 2%.

The data in Fig. 2 show that in accord with the earlier findings of the authors[1], the optical density decreased progressively with the addition of excess of versenate till the entirety of Cu^{+2} was chelated.

DISCUSSION

It is known that EDTA forms soluble complexes with most of the common metallic ions; SCHWARZENBACH and his coworkers[2,3] studied a number of complexes formed with versene and also compiled the stability constants thereof. The success of a method for determining the amount of a metallic ion using another ion as an indicator depends upon the circumstance that the indicator does not react during the course of the titration, but reacts with excess of the reagent[4] in such a way that a sudden change in a physical property, say the absorbancy, is brought in, which can be followed experimentally. As indicated above, this feature is controlled by the stability constants of the reactants operating at the equilibrium which exists at the equivalence point.

It is known that cupric ions in ammoniacal solution form a series of ammonia complexes from $[\mathrm{Cu(NH_3)}]^{+2}$ to $[\mathrm{Cu(NH_3)_5}]^{+2}$. BJERRUM[5] determined their relative proportions in different concentrations; the concentration of the complex $[\mathrm{Cu(NH_3)_5}]^{+2}$ increased rapidly as the concentration of $\mathrm{NH_3}$ approaches saturation[6]. From spectrophotometric and polarographic data the dissociation constant of $[\mathrm{Cu(NH_3)_5}]^{+2}$ has been calculated to be $1.35 \cdot 10^{-13}$ [7,8].

At the end-point of the titration of Ca^{+2} we have the following equilibrium:

$$[\mathrm{Cu(NH_3)_5}]^{+2} + \mathrm{CaY}^{-2} \rightleftarrows \mathrm{Ca}^{+2} + \mathrm{CuY}^{-2} + 5\mathrm{NH_3} \quad \ldots\ldots\ldots\ldots (1)$$

The equilibrium constant K_e is given by

$$K_e = \frac{[\mathrm{Ca}^{+2}]\,[\mathrm{CuY}^{-2}]\,[\mathrm{NH_3}]^5}{\left[[\mathrm{Cu(NH_3)_5}]^{+2}\right]\,[\mathrm{CaY}^{-2}]} = \frac{k_1\,k_3}{k_2}$$

where Y is the versenate ion and k_1, k_2 and k_3 are the dissociation constants of the following complexes:

$$k_1 = \frac{[\mathrm{Ca}^{+2}]\,[\mathrm{Y}^{-4}]}{[\mathrm{CaY}^{-2}]}\ ; \quad \mathrm{CaY}^{-2} \rightleftarrows \mathrm{Ca}^{+2} + \mathrm{Y}^{-4} \quad \ldots\ldots\ldots\ldots (2)$$

$$k_2 = \frac{[\mathrm{Cu}^{+2}]\,[\mathrm{Y}^{-4}]}{[\mathrm{CuY}^{-2}]}\ ; \quad \mathrm{CuY}^{-2} \rightleftarrows \mathrm{Cu}^{+2} + \mathrm{Y}^{-4} \quad \ldots\ldots\ldots\ldots (3)$$

$$k_3 = \frac{[\mathrm{Cu}^{+2}]\,[\mathrm{NH_3}]^5}{\left[[\mathrm{Cu(NH_3)_5}]^{+2}\right]}\ ; \quad [\mathrm{Cu(NH_3)_5}]^{+2} \rightleftarrows \mathrm{Cu}^{+2} + 5\mathrm{NH_3} \quad \ldots\ldots (4)$$

According to SCHWARZENBACH AND ACKERMAN[9], the dissociation constant of the calcium versenate complex (k_1) is $2.6 \cdot 10^{-11}$ and according to HUGHES AND MARTELL[10], the dissociation constant of copper versenate is $1.4 \cdot 10^{-16}$. These lead to a value of $2.5 \cdot 10^{-8}$ for K_e which is so small that the equilibrium represented by eq. (1) corresponds to the reaction proceeding almost completely to the left; the copper ions would not, therefore, react appreciably with calcium versenate. This is supported by the observation that no decrease in the absorbancy could be noticed during the titration of Ca^{+2} in the mixture (Fig. 2).

Beyond the end-point of Ca^{+2}, the following equilibrium applies:

$$[\mathrm{Cu(NH_3)_5}]^{+2} + \mathrm{Y}^{-4} \rightleftarrows \mathrm{CuY}^{-2} + 5\mathrm{NH_3}$$

the equilibrium constant being

$$K_e{}^1 = \frac{[\mathrm{CuY}^{-2}]\,[\mathrm{NH_3}]^5}{[\mathrm{Cu(NH_3)_5}{}^{+2}]\,[\mathrm{Y}^{-4}]} = \frac{k_3}{k_2}$$

References p. 573

Here K_e^1 is of the value $0.95 \cdot 10^{-3}$ which is sufficiently large enough to allow the reaction to proceed quantitatively to the right as soon as excess of versenate is present beyond the end-point of Ca^{+2}.

ACKNOWLEDGEMENT

The authors' thanks are due to Professor S. N. Gundu Rao, Director, and to Professor K. S. G. Doss, Professor of Sugar Chemistry, Indian Institute of Sugar Technology, for their kind interest in this work.

SUMMARY

Employing the absorption of the copper ammonium complex at $\lambda = 630$ mμ, a method for determining calcium with EDTA is described; an accuracy within 2% is obtainable. The use of the copper ammonium complex as an indicator in the titrations of calcium with EDTA has been elucidated from the knowledge of the stability constants of copper and calcium versenate and of the copper ammonium complex.

RÉSUMÉ

Une méthode est décrite pour le dosage du calcium au moyen de l'acide éthylènediaminetétra-acétique, en utilisant l'absorption du complexe amminé du cuivre à $\lambda = 630$ mμ. On peut arriver à une précision de 2%. L'emploi du complexe amminé du cuivre, comme indicateur pour les titrages du calcium avec l'EDTA s'explique lorsqu'on connaît les constantes de stabilité des complexes du cuivre et du calcium avec l'EDTA et celle du complexe amminé du cuivre.

ZUSAMMENFASSUNG

Eine Methode zur Bestimmung von Calcium mit EDTA wird beschrieben. Sie gründet sich auf die Messung der Absorption des Kupfer-Ammonium-Komplexes bei $\lambda = 630$ mμ; die Genauigkeit beträgt 2%. Die Anwendung des Kupfer-Ammonium-Komplexes als Indikator bei der Titration von Calcium mit EDTA wurde auf Grund der Kenntnis der Stabilitätskonstanten von Kupfer- und Calciumversenat und des Kupfer-Ammonium-Komplexes erklärt.

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A U.V. SPECTROPHOTOMETRIC DETERMINATION OF ELEMENTAL SULPHUR*

by

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INTRODUCTION

Some years ago HEATLY AND PAGE[1] published a U.V. spectrophotometric determination of elemental sulphur in ethanol. Lambert-Beer's law was obeyed at concentrations up to 40 μg of sulphur per ml. However, the method was interfered with by the presence of hydrogen sulphide, sulphate, thiosulphate, etc. Since elemental sulphur can be separated from these interfering substances by extraction with a solvent, which is not miscible with water, it was investigated whether elemental sulphur can be determined U.V. spectrophotometrically in such a solvent.

The spectra of sulphur in ethanol and hexane and in chloroform have been recorded by BAER AND CARMACK[2] and KOCH[3] respectively. These authors did not make use of these spectra to the determination of sulphur.

EXPERIMENTAL

Preliminary experiments

The spectrum of sulphur in petroleum ether was measured (Fig. 1) and shows a maximum absorptivity at a wavelength of 265 mμ. This may be considered to be in good agreement with the observations of HEATLEY AND PAGE[1], made on sulphur in ethanol. These authors found maximum absorptivity at 264 mμ. Also the spectrum of sulphur in n-hexane was determined (Fig. 2); again maximum absorptivity occurs at 264 mμ. Moreover, the absorptivity is practically constant between 272 mμ and 278 mμ, which was also found by BAER AND CARMACK[2].

As it is preferable to measure absorbances in a region, where the absorptivity is practically constant, it was decided to investigate whether the relation between absorbance at 276 mμ and concentration of sulphur in n-hexane is such that sulphur can be determined spectrophotometrically in n-hexane. From a few experiments it followed that the regression of absorbance on concentration was practically linear.

It is not possible to use every commercial grade of n-hexane. Evidently, the absorbance of n-hexane itself must be as small as possible at the wavelength chosen. It was found to be necessary to use n-hexane specially purified for the purpose. Spectrograde n-hexane of Messrs. HOPKIN AND WILLIAMS is satisfactory. The absorbances of this n-hexane at different wavelengths, measured in a 1 cm-cell against distilled water as a blank, using a Unicam SP 500 spectrophotometer, are given in Table I.

Calibration graph

After these preliminary experiments the calibration graph was established. Sublimed sulphur was chosen as a starting material and was washed with water until the filtrate was free from both acid

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* Part of the thesis of M. J. MAURICE, Dissertation Free University, Amsterdam, 1956.

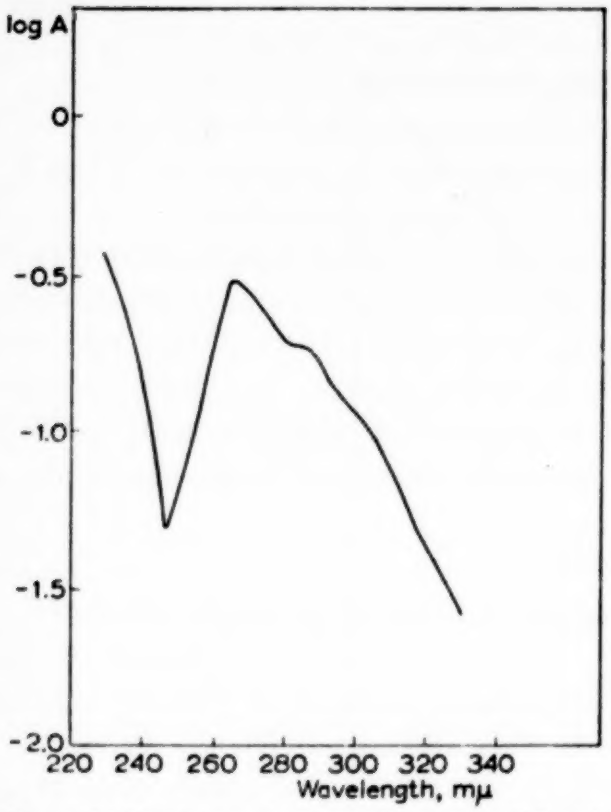

Fig. 1. U.V. absorption spectrum of sulphur in petroleum ether.

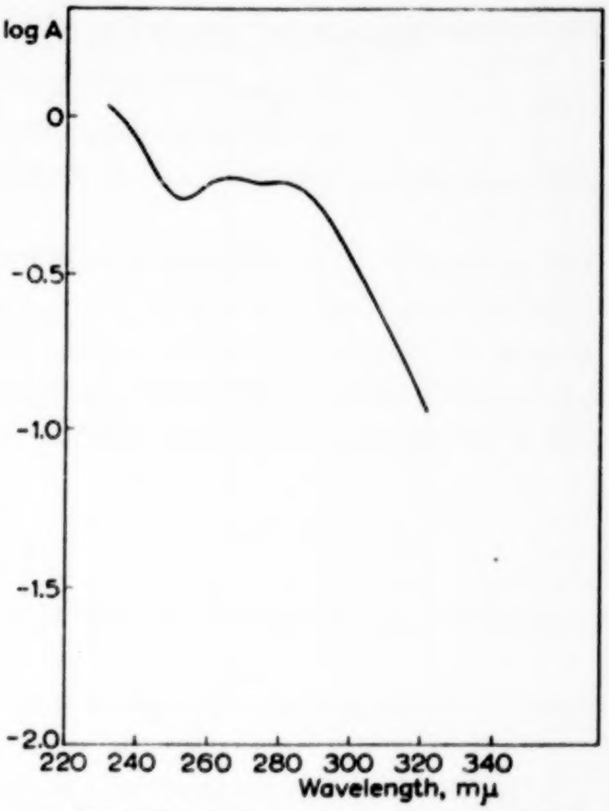

Fig. 2. U.V. absorption spectrum of sulphur in n-hexane.

TABLE I

Wavelength mμ	*Absorbance*	*Wavelength mμ*	*Absorbance*
220	0.280	265	0.142
230	0.210	270	0.066
240	0.410	280	0.024
250	0.840	290	0.022
260	0.365		

and any iodine-consuming substance. This purified sulphur was dried in an oven at 100°C for $1^1/_2$ hour. The content was determined by combustion to sulphur dioxide, which was converted into sulphuric acid and determined as such according to GOUVERNEUR AND VAN DIJK[4]. The determination was carried out in fourfold and the mean content found was 99.73%. The standard deviation of an individual determination was 0.05%.

A known amount of this sulphur was dissolved in n-hexane of spectrograde quality. Eight different aliquots of this stock-solution were diluted with n-hexane. At each of these eight concentrations five different solutions were prepared. The absorbances at a wavelength of 276 mμ of these 40 solutions were measured against spectrograde n-hexane as a blank, using a Unicam SP 500 spectrophotometer and 1 cm-cells.

The mean absorbances measured at each concentration and the standard deviation of an individual measurement are given in Table II.

TABLE II

Concentration μg/ml	*Mean absorbance*	*Standard deviation*
5	0.142	0.003
10	0.275	0.006
15	0.406	0.006
20	0.528	0.008
25	0.656	0.005
30	0.776	0.005
35	0.902	0.008
40	1.008	0.005

References p. 577

. The calibration graph is shown in Fig. 3.

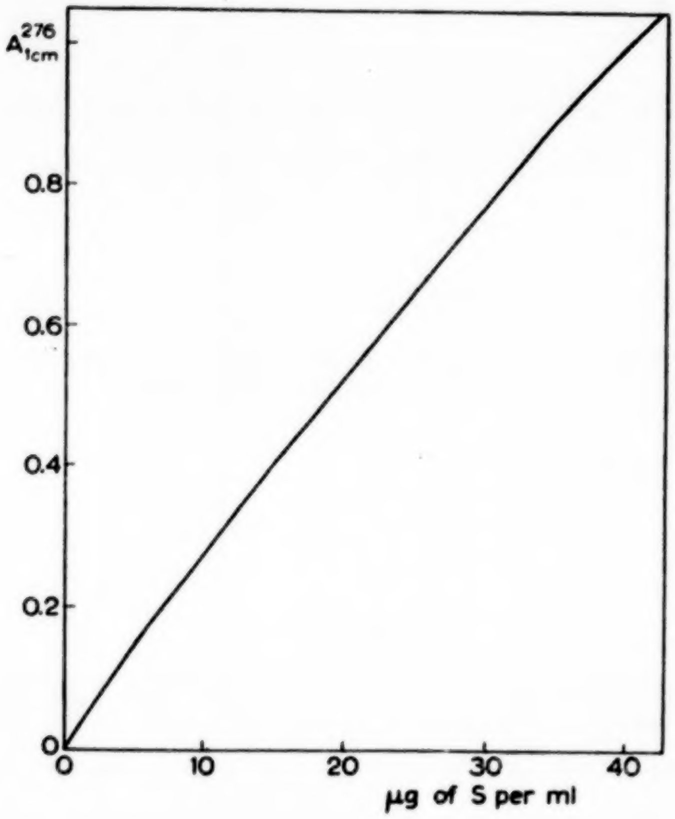

Fig. 3. Calibration graph for the determination of elemental sulphur in *n*-hexane.

The relationship between absorbance and concentration was supposed to be linear. Since the error in concentration is negligible compared with that in absorbance, this relationship can be estimated by computing the regression of absorbance on concentration by application of the method of least squares.

The equation proved to be: $A = 0.0274 + 0.02485\,C$.

By application of the t-test it was established that the intercept differs significantly from zero on the 1-% level. However, since all measurements were carried out against a blank of the solvent, the intercept of the graph must be zero. Therefore, the equation of the calibration graph was assumed to be quadratic and to obey the general relationship $A = \mathrm{a}C + \mathrm{b}C^2$. It must be remarked that it can also be seen from Table II that the graph is not a straight line. Calculating the coefficients a and b, the following equation was found: $A = 0.0284\,C - 0.000082\,C^2$.

The equation of the calibration graph was calculated since the graphic determination of the concentration from the absorbance measured is less precise than the determination with the aid of the equation. Also for the prediction of the precision of the spectrophotometrically determined concentration it is necessary to calculate the equation of the graph.

PRECISION OF THE METHOD

The exact calculation of the standard deviation of the spectrophotometrically determined concentration on the basis of the formula $A = \mathrm{a}C + \mathrm{b}C^2$ involves many difficulties. To simplify it, the calibration graph was considered to be a straight line for this purpose. In this way an approximate upper bound for this standard deviation is found. The variance of the concentration, C_0 reported, which is calculated from the measured absorbance with the aid of the formula $A_0 = \mathrm{a} + \mathrm{b}C_0$, is given by:

$$\mathrm{Var}(C_0) = \frac{\mathrm{Var}(A)}{\mathrm{b}^2}\left\{1 + \frac{1}{n} + \frac{(A_0 - \bar{A})^2}{\mathrm{b}^2 \Sigma (C_i - \bar{C})^2}\right\}$$

where n = the number of measurements involved in establishing the calibration graph.

$\bar{A}$ = average of all absorbances measured in establishing the graph.
$\bar{C}$ = average of all concentrations used in deriving the graph.
A_0 = absorbance measured at the unknown concentration C_0.
Var(A) = variance of the absorbance, calculated in deriving the equation of the calibration graph.

It is evident that Var(C_0) is a function of A_0 and thus a function of C_0. However, the coefficients of C_0 and C_0^2 in the formula for Var(C_0) are so small, that it is allowed to consider Var(C_0) to be independent from C_0 for C_0-values within the range of concentrations examined, *i.e.* from 5 to 40 µg of sulphur per ml. Application of the formula for Var(C_0) gives a standard deviation of 0.23 µg of sulphur per ml. The precision of the method, therefore, is very satisfactory.

CONCLUSIONS

From the experiments and calculations described above, the following conclusions can be drawn:

1. It is possible to determine elemental sulphur in *n*-hexane in concentrations from 5 to 40 µg per ml by measurement of the absorbance at 276 mµ.
2. It is necessary to use *n*-hexane of spectrograde quality for this determination.
3. The calibration graph of elemental sulphur in *n*-hexane is quadratic. Therefore, it is impossible to calculate the molar absorptivity of sulphur in *n*-hexane at 276 mµ.
4. The standard deviation of an individual determination amounts to maximum 0.23 µg of sulphur per ml.

RECOMMENDED PROCEDURE

Dissolve the amount of elemental sulphur to be determined in *n*-hexane of spectrograde quality and dilute with *n*-hexane to a concentration of 5 to 40 µg per ml. Measure the absorbance of this solution at a wavelength of 276 mµ against a blank of the solvent using 1-cm cells. Calculate the concentration from the absorbance measured with the aid of an equation for the calibration graph, prepared in the same way, starting from known amounts of pure sulphur.

ACKNOWLEDGEMENT

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SUMMARY

A U.V. spectrophotometric determination of elemental sulphur in *n*-hexane is described and the precision of the method is calculated.

RÉSUMÉ

Une méthode spectrophotométrique U.V. est décrite pour le dosage du soufre élémentaire; la précision de la méthode a été calculée.

ZUSAMMENFASSUNG

Eine U.V. spektrophotometrische Bestimmung von Elementarschwefel wird beschrieben und die Präzision der Methode wird berechnet.

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A COMPARISON OF THREE METHODS FOR THE DETERMINATION OF COLLOIDAL SULPHUR*

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INTRODUCTION

In an investigation into the determination of elemental sulphur in rayon it was necessary to study this determination itself in the first place.

For the determination of elemental sulphur a few methods are known. According to HALL[1,2] and PROSKE[3,4] elemental S can be determined polarographically. MORRIS *et al.*[5] founded a method on the conversion of sulphur into thiosulphate by boiling the sulphur with sulphite. The thiosulphate formed is then titrated. BARTLETT AND SKOOG[6] state a spectrophotometric determination of sulphur after conversion into thiocyanate, while HEATLY AND PAGE[7] found that ethanolic solutions of elemental sulphur show a strong absorption in the u.v. region of the spectrum and that sulphur can be determined in this solvent by measurement of the absorbance at a wavelength of 264 mμ. Elemental sulphur can also be determined by reduction to sulphide[8,9] and by oxidation to sulphate[10].

For our purpose we wanted a simple and — if possible — quick method for the determination of elemental sulphur. It was decided to study three principles for this determination and to compare the results, whereby special attention was paid to accuracy and precision. As starting material a solution of colloidal sulphur was taken. The three principles chosen were:

1. oxidation with alkaline permanganate and titration of the excess permanganate,
2. reduction to sulphide with zinc and hydrochloric acid and complexometric determination of sulphide,
3. formation of thiosulphate by boiling with sulphite and titration of the thiosulphate formed.

EXPERIMENTAL PART

A standard solution of colloidal sulphur was prepared from sodium thiosulphate and sulphuric acid according to RAFFO[11]. The solution obtained did not consume any 0.01N I_2. The content of this solution was determined by oxidation with alkaline permanganate according to procedure 1[12].

Procedure 1

Add 5 ml of the solution of colloidal sulphur, containing 5 to 10 mg of sulphur, to 50 ml of 0.1N potassium permanganate and 25 ml of 10N sodium hydroxide. Heat the solution for 10 to 15 minutes to 40-45°C and after cooling acidify with 25 ml of sulphuric acid (1 + 1). Add 50 ml of $0.12N$ oxalic acid and, if the solution turns turbid, 20 ml of $MnSO_4$ solution (50 g of $MnSO_4 \cdot 4\,H_2O$ per litre). If it remains clear, omit the $MnSO_4$ addition. Heat the solution to 50-60°C and titrate the excess oxalic acid with $0.1N$ $KMnO_4$ until a faint pink persists.

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* Part of the thesis of M. J. MAURICE, Dissertation Free University, Amsterdam, 1956.

Further, the standard solution was analyzed according to procedure 2.

Procedure 2

Introduce into the distillation apparatus (Fig. 1) an aliquot of the standard colloidal S solution containing 1 to 10 mg of sulphur, and connect the apparatus with three gas-wash bottles, the first containing 25 ml of $4N$ H_2SO_4 and the other two containing each 25 ml of $0.02N$ copper(II) acetate in $0.5N$ acetic acid. Add to the S-solution 5 g of As-free zinc and pass a stream of nitrogen through the apparatus. After 15 minutes add 25 ml of $5N$ HCl and reduce for one hour in the cold. Then boil the solution for 10 minutes, the H_2S evolved being absorbed in the copper(II) acetate solution. Disconnect the gas-wash bottles from the distillation flask and transfer the contents of the last two bottles quantitatively to a 200-ml volumetric flask. Make up to volume with distilled water and filter off the precipitate, rejecting the first 25 ml of the filtrate. Add to 100 ml of the filtrate 2 ml of 1% tartaric acid solution, 100 mg of murexide indicator (200 mg of murexide ground in a mortar with 50 g of anhydrous analytical grade NaCl) and so much $4N$ NH_4OH that the colour changes to green. Then add three more drops of $4N$ NH_4OH and titrate with $0.02N$ disodium salt of ethylenediamine tetraaceticacid (versenate), till the colour changes to violet.

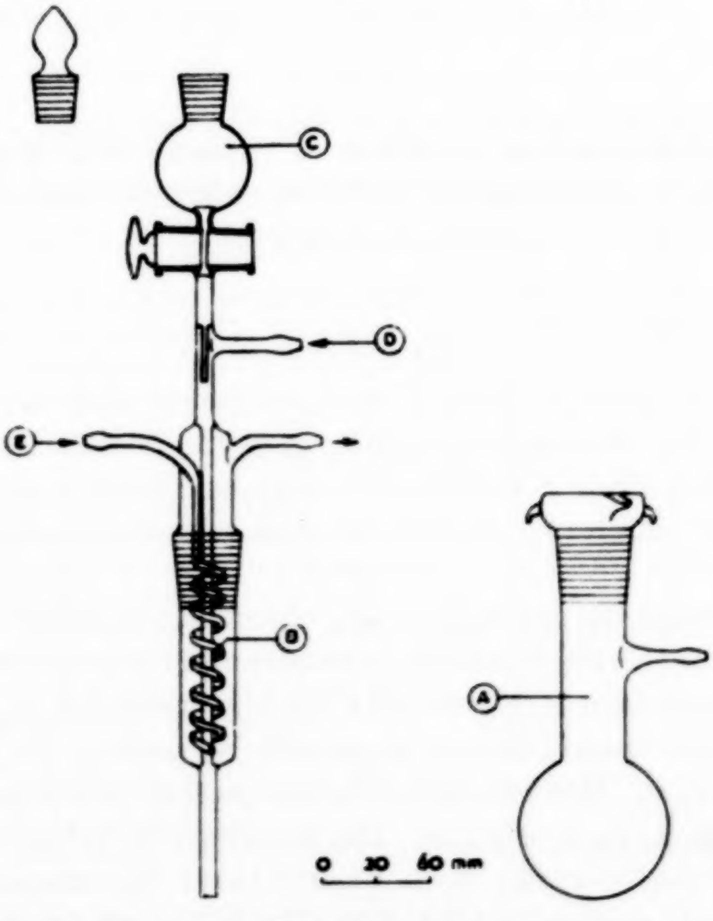

Fig. 1. Distillation apparatus. A: 250-ml flask, B: spiral condenser, C: funnel, D: nitrogen inlet, E: water inlet.

From preliminary experiments it could be shown that the results of the reduction with zinc and HCl are affected by the acidity of the S solution during the reduction. Quantitative results are obtained when the acidity is 4.5 to $5N$. At lower acid concentrations low results are found.

The third method tested was procedure 3.

Procedure 3

Add an aliquot of the standard colloidal S solution containing 1 to 10 mg of sulphur to 25 ml of $0.5N$ Na_2SO_3 and heat on a steambath for 30 minutes. After cooling add 40 ml of 40% formaldehyde solution and neutralize with $1N$ sulphuric acid, using one drop of methyl orange as an indicator.

Titrate with 0.01 *N* iodine solution, using starch as an indicator, until the colour of the solution is just violet-blue. In the same way carry out a blank determination, omitting the addition of the colloidal sulphur solution.

According to procedure 1 sixteen determinations were carried out. According to procedures 2 and 3 twenty-four determinations were carried out, starting from three different aliquots of the standard solution. The blank determination, required in procedure 3, was carried out in eightfold. The results are given in Table I, where $\bar{x}_1$, $\bar{x}_2$ and $\bar{x}_3$ are the average results of the determinations according to procedures 1, 2 and 3, respectively, and n is the number of determinations.

TABLE I

$\bar{x}_1$	n	$\bar{x}_2$	n	$\bar{x}_3$	n
3.930 mg of S		3.92 mg of S	8		
5.240 ,,	16	5.21 ,,	8		
7.865 ,,		7.85 ,,	8		
2.370 mg of S				2.09 mg of S	8
4.745 ,,	16			4.21 ,,	8
7.115 ,,				6.25 ,,	8

For each method the standard deviation of an individual determination was calculated. These standard deviations are 0.059 mg of S, 0.080 mg of S and 0.13 mg of S, respectively, for procedures 1, 2 and 3, in that order.

DISCUSSION

The average results, given in Table I, were compared with each other with the aid of the t-test. In this way, no significant differences can be detected between the results of procedure 1 and procedure 2. Between the standard deviations found for these procedures no significant difference is to be assumed, which is established by application of the F-test.

The difference between the average results, obtained according to procedures 1 and 3 is highly significant on the 1% level. The results found for procedure 3 are consistently low. However, the dispersion of the recovery, *i.e.* the quotient $\bar{x}_3/\bar{x}_1$, is caused by chance fluctuations only. This means that it is possible to correct the results obtained by multiplication with $\bar{x}_1/\bar{x}_3$. This correction factor must of course be determined experimentally. In our case $\bar{x}_1/\bar{x}_3$ equals 1.15. The standard deviation, *viz.* 0.13 mg of S, is rather high, which is partly due to the fact that a blank determination is required. This may be explained by assuming that the excess Na_2SO_3 is not masked quantitatively by addition of formaldehyde. The differences between the standard deviation and those found for procedures 1 and 2 are significant on the 5% level. This means that the results obtained according to procedure 3 are less precise than those obtained according to procedures 1 and 2.

The fact that MORRIS *et al.*[5] obtained higher results than we found must be partly ascribed to the omission of the blank determination by these authors. In this case of the determination of colloidal sulphur, the recovery found for procedure 3, *viz.* 87%, could not be increased by addition of alkyl pyridinium chloride to the mixture of colloidal sulphur and sulphite as suggested by LEVENSON[13].

Thus, several objections against procedure 3 were found: poor precision, the necessity of a blank determination and the fact that the results must be corrected by multiplication with an empirical factor.

The conclusion that procedures 1 and 2 yield accurate results and that procedure 3 yields too low results is allowed, because the volumetric standard solutions used in each of the procedures, *viz.* $KMnO_4$, versenate and iodine, were standardized in independent ways with the aid of oxalic acid, analytical grade copper(II) acetate and potassium dichromate respectively. The three methods investigated, therefore, are fully independent.

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SUMMARY

Three methods for the determination of colloidal sulphur are described and the results obtained are compared. Serious objections were found against the method based on the formation of thiosulphate by boiling sulphur with sulphite and titration of thiosulphate.

RÉSUMÉ

Trois méthodes pour le dosage du soufre colloïdal sont décrites et les résultats obtenus sont comparés. La méthode, basée sur la formation de thiosulfate, par ébullition du soufre avec un sulfite et titrage du thiosulfate formé, présente des inconvénients.

ZUSAMMENFASSUNG

Drei Methoden für die Bestimmung kolloidalen Schwefels werden beschrieben und die erhaltenen Resultate werden verglichen. Ernsthafte Einwände wurden gegen die Methode gefunden, welche auf der Bildung von Thiosulphat durch Kochen von Schwefel mit Sulphit und Titration von Thiosulphat basiert ist.

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RÉDUCTION ÉLECTROCHIMIQUE DE L'EAU ET DE SES IONS. I.

par

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En milieu aqueux, l'étude des oxydants et des réducteurs est limitée du côté des potentiels négatifs soit par la réduction des ions hydrogène, soit par la réduction de l'eau. L'expérience montre, qu'en présence d'une électrode donnée, la position des courbes de polarisation de l'eau et de ses ions dépend du pH. Nous avons étudié systématiquement ce phénomène en présence de platine platiné.

L. R. FRESENIUS[1] a montré que les ions hydrogène sont réductibles en présence de platine platiné et mis en évidence un palier de diffusion dont la hauteur est proportionnelle à leur concentration. Mais la position relative des courbes de polarisation en fonction du pH n'a pas grande signification car l'auteur n'a pas utilisé d'électrode de référence (anode de platine poli).

PARTIE THÉORIQUE

Dans tout ce qui suit, nous supposons, comme le justifient nos résultats expérimentaux, que toutes les réactions électrochimiques en présence de platine platiné sont rapides.

Nous admettons et nous vérifions plus loin que, suivant la nature des ions en solution et le potentiel considéré, deux réactions électrochimiques distinctes sont possibles à savoir:

(1) réduction des ions hydrogène

$$2\ H^+ + 2e \rightleftarrows H_2$$

(2) réduction de l'eau

$$2\ H_2O + 2e \rightleftarrows H_2 + 2\ OH^-$$

Cette hypothèse a déjà été avancée sous différentes formes par quelques auteurs[2,3].

Nous considérons ici H_2O comme un complexe de H^+, complexe très stable dont les vitesses de dissociation et de recombinaison sont suffisamment grandes devant les vitesses de réaction à l'électrode pour ne pas intervenir dans la cinétique du processus électrochimique. Cette condition sera vérifiée plus loin par ses conséquences expérimentales.

Nous allons établir l'équation des courbes de polarisation (1) et (2) en supposant négligeable le phénomène de migration des ions électroactifs. Cette condition est réalisée

Bibliographie p. 591

expérimentalement en utilisant un électrolyte indifférent suffisamment concentré. L'intensité du courant est alors déterminée par la diffusion des espèces réagissant à l'électrode.

Cas 1

$$2\,H^+ + 2e \rightleftarrows H_2 \quad \ldots\ldots\ldots\ldots \quad (1)$$

En supposant: — cette réaction électrochimique rapide,

— les concentrations égales aux activités, le potentiel d'électrode est donné par la relation de Nernst.

$$E = E_\circ + \frac{0.059}{2} \log \frac{[H^+]_e^2}{[H_2]_e}$$

Dans cette équation, $E_\circ$ est le potentiel normal d'équilibre de la réaction (1), $[H^+]_e$ et $[H_2]_e$ les concentrations des ions hydrogène et de l'hydrogène dissous au voisinage de l'électrode.

D'autre part:

$$\begin{aligned} i &= k_{H^+}([H^+]_e - [H^+]_s) \\ i &= k_{H_2}([H_2]_s - [H_2]_e) \\ i_{H^+} &= -k_{H^+}[H^+]_s \\ i_{H_2} &= k_{H_2}[H_2]_s \end{aligned}$$

Dans ces équations, i représente l'intensité du courant, négative pour un courant de réduction (cathodique), positive pour un courant d'oxydation (anodique);

i_{H^+} et i_{H_2} les intensités des courants de diffusion;

k_{H^+} et k_{H_2} les coefficients de diffusion;

$[H^+]_s$ et $[H_2]_s$ les concentrations au sein de la solution des ions hydrogène et de l'hydrogène dissous.

Donc:

$$E = E_\circ + \frac{0.059}{2} \log \frac{k_{H_2}}{(k_{H^+})^2} + \frac{0.059}{2} \log \frac{(i - i_{H^+})^2}{i_{H_2} - i} \quad \ldots\ldots\ldots\ldots \quad (1)$$

Cas 2

$$2\,H_2O + 2e \rightleftarrows H_2 + 2\,OH^-$$

En utilisant les mêmes hypothèses, conventions et symboles que précédemment:

$$E = E_\circ' - \frac{0.059}{2} \log [OH^-]_e^2[H_2]_e$$

$$\begin{aligned} i &= k_{OH^-}([OH^-]_s - [OH^-]_e) \\ i &= k_{H_2}([H_2]_s - [H_2]_e) \\ i_{OH^-} &= k_{OH^-}[OH^-]_s \\ i_{H_2} &= k_{H_2}[H_2]_s \end{aligned}$$

d'où:

$$E = E_\circ' + \frac{0.059}{2} \log (k_{OH^-})^2 k_{H_2} - \frac{0.059}{2} \log (i_{OH^-} - i)^2(i_{H_2} - i)$$

$E_\circ$ et $E_\circ'$ ne sont pas indépendants; en effet, si nous supposons que les vitesses de dissociation et de recombinaison de H_2O sont grandes devant les vitesses des réactions électrochimiques mises en jeu, il y a équilibre chimique des ions présents au voisinage de l'électrode soit:

$$[H^+]_e[OH^-]_e = K_{H_2O}$$

K_{H_2O} désignant le produit ionique de l'eau.

Bibliographie p. 591

En chaque point de la courbe de polarisation, le potentiel d'électrode vérifie les équations de Nernst:

$$E = E_\circ + \frac{0.059}{2} \log \frac{[\mathrm{H}^+]_e^2}{[\mathrm{H}_2]_e} = E_\circ' - \frac{0.059}{2} \log [\mathrm{OH}^-]_e^2[\mathrm{H}_2]_e$$

d'où:

$$\begin{aligned} E_\circ' &= E_\circ - 0.059 \, \mathrm{p}K_{\mathrm{H_2O}} \\ &= E_\circ - 0.82 \text{ volt à } 20\,^\circ\mathrm{C} \end{aligned}$$

Donc:

$$E = E_\circ - 0.059 \, \mathrm{p}K_{\mathrm{H_2O}} + \frac{0.059}{2} \log [k_{\mathrm{OH}^-}]^2 k_{\mathrm{H}_2} - \frac{0.059}{2} \log (i_{\mathrm{OH}^-} - i)^2 (i_{\mathrm{H}_2} - i) \quad \ldots\ldots \quad (2)$$

En milieu acide et neutre, $[\mathrm{OH}^-]_s$ est très faible donc i_{OH^-} est négligeable devant i et en l'absence d'hydrogène:

$$E = C - 3 \frac{0.059}{2} \log (-i)$$

La position de la courbe de réduction de l'eau est alors indépendante du pH. Ce résultat a déjà été obtenu expérimentalement en présence d'autres électrodes[4,5] que celle de platine platiné.

PARTIE EXPÉRIMENTALE

Montage

Nous avons utilisé le montage classique à trois électrodes comprenant:

— un circuit d'électrolyse,

— un circuit de mesure du potentiel de l'électrode indicatrice.

Le galvanomètre du circuit d'électrolyse est un appareil SEFRAM type LTA I qui permet de mesurer des intensités de courant comprises entre 0.05 et 1500 μA (sensibilité maximum: 0.0025 μA/mm).

Le potentiomètre du circuit de mesure est un appareil MECI type VS qui permet de mesurer des différences de potentiel comprises entre —1400 et +1400 mV à 1 mV près.

Électrodes

L'électrode indicatrice est un fil de platine platiné soudé à l'extrémité d'un tube de verre. L'âme de platine a environ 0.8 mm de diamètre et 5 mm de longueur.

Le platinage est réalisé électrolytiquement (anode de platine poli). Composition du bain électrolytique: 30 ml eau distillée, 1 g tétrachlorure de platine, 8 mg acétate de plomb. Densité de courant: 0.06 A/cm^2; durée 5 min.

L'électrode indicatrice est replatinée avant chaque expérience.

L'électrode de référence est un fil d'argent recouvert de chlorure d'argent et plongé directement dans la solution.

Cellule d'électrolyse

Une tubulure permet d'envoyer un courant gazeux dans les solutions

— soit un courant d'azote (contenant moins de 0.1% d'oxygène) afin d'éliminer l'oxygène dissous;

— soit un courant d'hydrogène préalablement débarrassé d'oxygène par barbotage dans une solution de sulfate vanadeux.

La solution est agitée à l'aide d'un agitateur magnétique dont l'aimant tourne à une vitesse sensiblement constante.

RÉSULTATS EXPÉRIMENTAUX

I. En l'absence d'hydrogène

Nous avons tout d'abord étudié la réduction de l'eau et de ses ions en l'absence d'hydrogène (faisceau de courbes de la Fig. 1).

a. ***En milieu neutre***, en l'absence d'une quantité notable d'ions hydrogène en solution, seule la réduction directe de l'eau est possible (réaction (2)); la courbe de polarisation

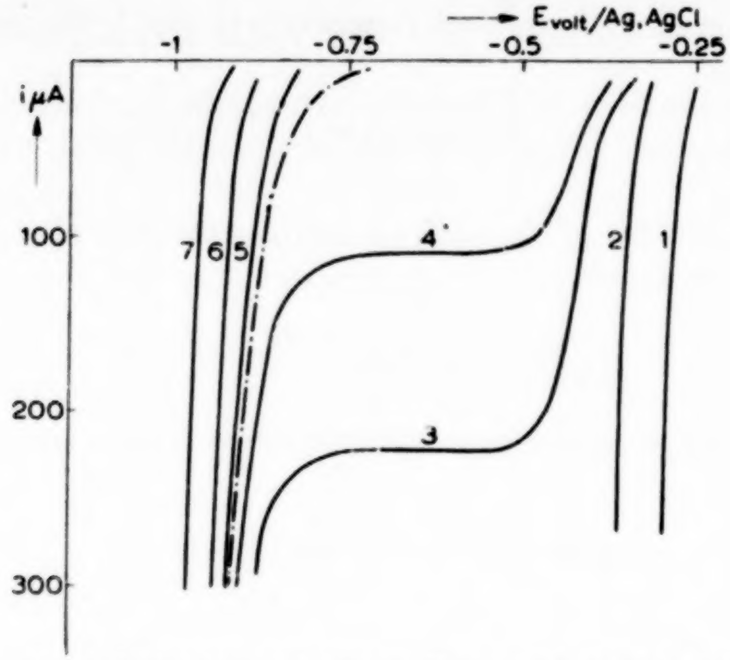

Fig. 1. Courbes de polarisation cathodique. En traits mixtes solution NaCl M;
Courbe 1: solution HCl env. 0.1M, NaCl M, pH 0.9;
Courbe 2: solution HCl env. 0.01M, NaCl M, pH 1.9;
Courbe 3: solution HCl env. 0.001M, NaCl M, pH 2.8;
Courbe 4: solution HCl env. 0.0005M, NaCl M, pH 3.2;
Courbe 5: solution NaOH env. 0.001M, NaCl M, pH 10.6;
Courbe 6: solution NaOH env. 0.01M, NaCl M, pH 11.7;
Courbe 7: solution NaOH env. 0.1M, NaCl M, pH 12.6;
Atmosphère d'azote. Electrode de platine platiné.

cathodique d'une solution de chlorure de sodium moléculaire est figurée en traits mixtes.

L'équation de cette courbe d'après les calculs développés plus haut est:

$$E = A - \frac{0.059}{2} \log (i_{OH^-} - i)^2(-i)$$

Or, i_{OH^-} est ici négligeable devant i car la concentration des ions hydroxyde en solution est très faible, donc:

$$E = A - 3\,\frac{0.059}{2} \log (-i)$$

Nous avons étudié la fonction $E = f[\log(-i)]$. La courbe expérimentale obtenue (Fig. 2) est une droite de coefficient angulaire —99 mV/unité de log (valeur théorique à la température ordinaire: —90 mV/unité de log).

b. *En solution fortement acide* (courbes 1 et 2 de la Fig. 1) a lieu la réduction directe des ions hydrogène (réaction (I)). Cette réduction dépend du pH du milieu.

En solution faiblement acide, il est possible de mettre en évidence la réduction successive des ions hydrogène et de l'eau. Les courbes 3 et 4 de la Fig. 1 présentent un palier dont la hauteur est proportionnelle à la concentration des ions hydrogène en solution et une partie rapidement ascendante se confondant avec la courbe obtenue en milieu neutre: cette partie correspond à la réduction directe de l'eau.

L'équation de ces courbes d'après les calculs développés plus haut est de la forme:

$$E = B + \frac{0.059}{2} \log \frac{(i - i_{H^+})^2}{(-i)}$$

Lorsque la solution est suffisamment concentrée en ions hydrogène, *i* est négligeable devant i_{H^+} et:

$$E = B - 0.059\ \text{pH} - \frac{0.059}{2} \log(-i)$$

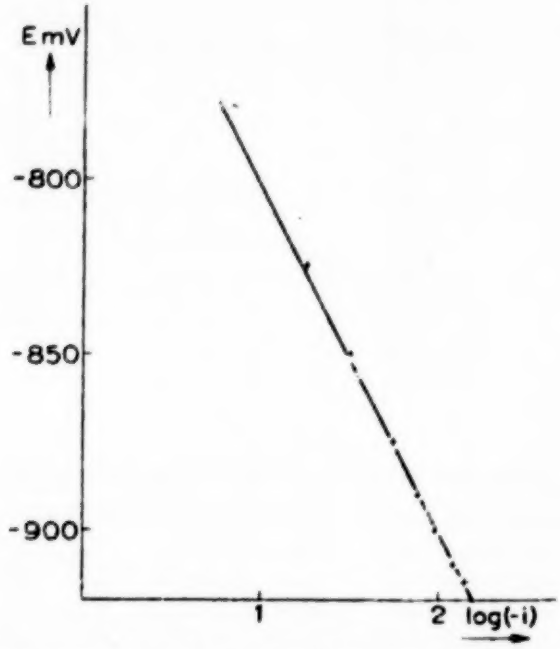

Fig. 2. Réduction d'un solution NaCl *M*. Coefficient angulaire: —99 mV/unité de log.

Nous avons étudié la fonction $E = f[\log(-i)]$ pour une solution d'acide chlorhydrique 0.1 *M*. La courbe obtenue (Fig. 3) est une droite de coefficient angulaire —32 mV/unité de log (valeur théorique à la température ordinaire: —30 mV/unité de log).

Lorsque la concentration des ions hydrogène dans la solution est telle que *i* et i_{H^+} sont du même ordre de grandeur

$$E = B + \frac{0.059}{2} \log \frac{(i - i_{H^+})^2}{(-i)}$$

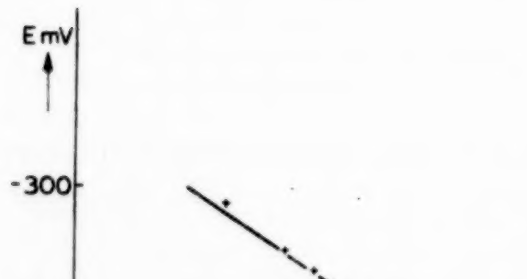

Fig. 3. Réduction d'une solution HCl env. 0.1 *M*, NaCl *M*. Coefficient angulaire: —32 mV/unité de log.

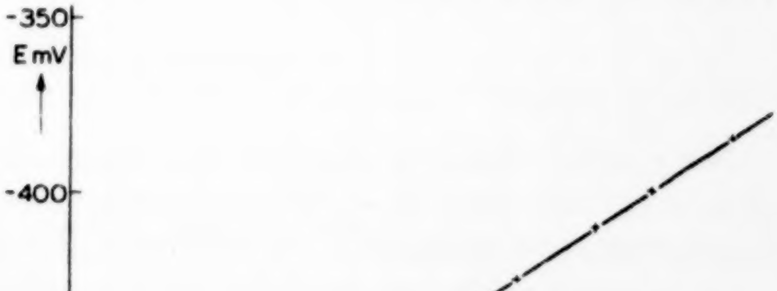

Fig. 4. Réduction d'une solution HCl env. 0.001 *M*, NaCl *M*. Coefficient angulaire: 32 mV/unité de log.

Bibliographie p. 591

Nous avons étudié la fonction $E = \mathrm{f}\left[\log\frac{(i - i_{\mathrm{H}^+})^2}{(-i)}\right]$ pour une solution d'acide chlorhydrique 0.001 M. La courbe expérimentale obtenue (Fig. 4) est une droite de coefficient angulaire 32 mV/unité de log (valeur théorique à la température ordinaire 30 mV/unité de log).

c. *En milieu alcalin*, la réduction directe de l'eau intervient seule et est fonction du pH (Courbes 5, 6 et 7 de la Fig. 1). L'équation de ces courbes est de la forme:

$$E = A - \frac{0.059}{2}\log(i_{\mathrm{OH}^-} - i)^2(-i)$$

Lorsque la solution est suffisamment concentrée en ions hydroxyde, i est négligeable devant i_{OH^-} et:

$$E = A - 0.059\,\mathrm{pH} - \frac{0.059}{2}\log(-i)$$

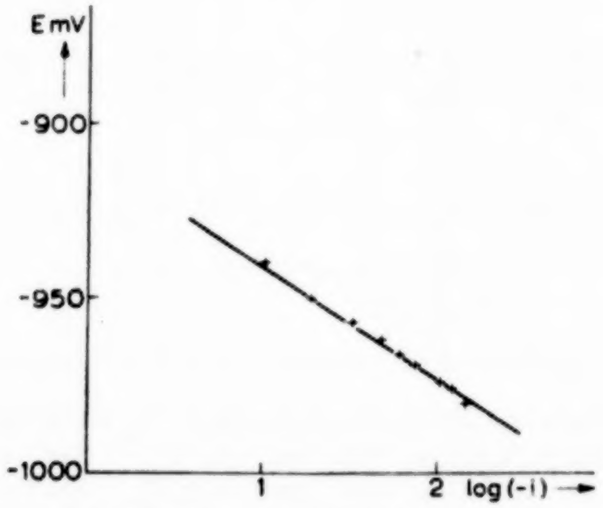

Fig. 5. Réduction d'une solution NaOH env. 0.1 M, NaCl M. Coefficient angulaire: —32 mV/unité de log.

La fonction $E = \mathrm{f}[\log(-i)]$ a été étudiée pour une solution de soude 0.1 M. La courbe expérimentale obtenue (Fig. 5) est une droite de pente —32 mV/unité de log (valeur théorique à la température ordinaire: —30 mV/unité de log).

Remarque: Ces résultats permettent d'envisager un dosage ampérométrique de petites quantités d'ions H^+ libres, utilisant comme électrode indicatrice une électrode de platine platiné.

2. *En présence d'hydrogène*

Nous avons étudié également la réduction de l'eau et de ses ions dans des solutions saturées d'hydrogène à la pression atmosphérique (Fig. 6). Cette figure montre les vagues d'oxydation anodique de l'hydrogène dissous en différents milieux. La présence d'hydrogène en solution permet de mettre en évidence les différentes possibilités de limitation de l'intensité anodique prévues par le calcul.

a. Soit le cas d'une *solution neutre non-tamponnée* (courbes en traits mixtes de la Fig. 6).

α. La réduction de l'eau a lieu suivant la réaction (2):

$$2\,H_2O + 2e \rightleftarrows H_2 + 2\,OH^-$$

Bibliographie p. 591

il n'y a pas de limitation de l'intensité cathodique. Le calcul conduit à l'équation suivante de la courbe cathodique:

$$E = A - \frac{0.059}{2} \log (-i)^2(i_{H_2} - i)$$

Expérimentalement, les variations de E en fonction de log $(-i)^2(i_{H_2} - i)$ sont linéaires: la droite obtenue a pour coefficient angulaire —33 mV/unité de log (Fig. 7) (valeur théorique —30 mV/unité de log).

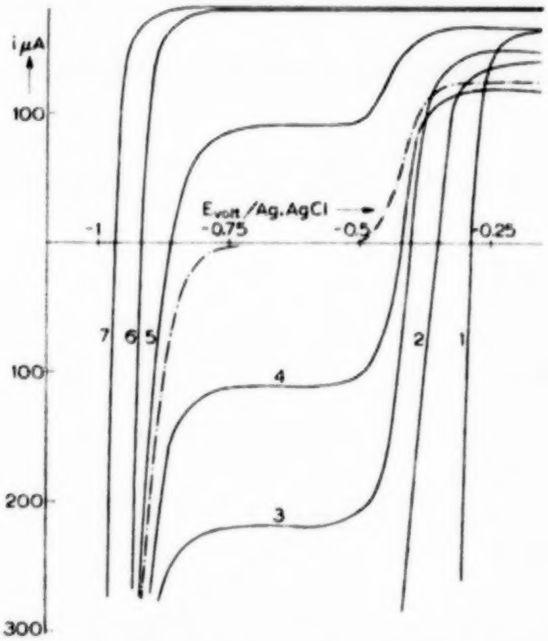

Fig. 6. Courbes de polarisation anodique et cathodique. En traits mixtes solution NaCl M;
Courbe 1: solution HCl env. 0.1 M, NaCl M;
Courbe 2: solution HCl env. 0.01 M, NaCl M;
Courbe 3: solution HCl env. 0.001 M, NaCl M;
Courbe 4: solution HCl env. 0.0005 M, NaCl M;
Courbe 5: solution NaOH env. 0.001 M, NaCl M;
Courbe 6: solution NaOH env. 0.01 M, NaCl M;
Courbe 7: solution NaOH env. 0.1 M, NaCl M;
Atmosphère d'hydrogène. Electrode de platine platiné.

β. L'oxydation de l'hydrogène suivant la réaction (2) est impossible car la concentration des ions hydroxyde en solution est trop faible; elle a lieu alors suivant la réaction (1):

$$H_2 \rightleftarrows 2\,H^+ + 2e$$

et le courant anodique est limité par la diffusion de H_2. Le calcul conduit à l'équation suivante de la courbe de polarisation anodique:

$$E = B + \frac{0.059}{2} \log \frac{i^2}{i_{H_2} - i}$$

Expérimentalement, les variations de E en fonction de log $\frac{i^2}{i_{H_2} - i}$ sont linéaires: la droite obtenue a pour coefficient angulaire 33 mV/unité de log (Fig. 8) (valeur théorique 30 mV/unité de log).

b. Dans le cas d'une *solution acide*, la réaction oxydo-réductrice à considérer est:

$$H_2 \rightleftarrows 2\,H^+ + 2e$$

Bibliographie p. 591

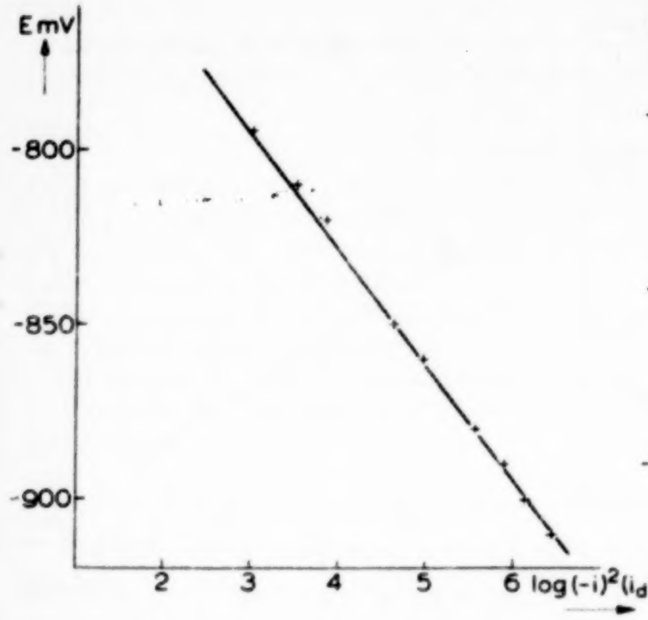

Fig. 7. Réduction d'une solution NaCl *M* saturée d'hydrogène. Coefficient angulaire: —30 mV/unité de log.

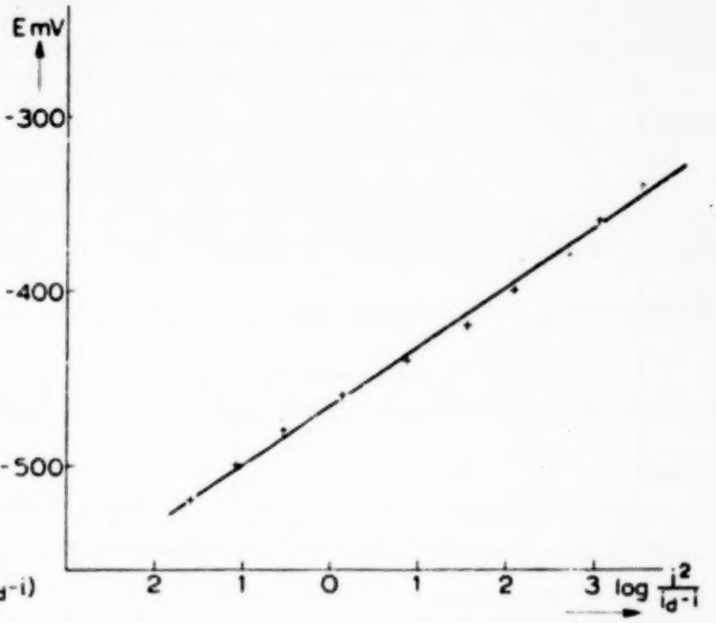

Fig. 8. Oxydation d'une solution NaCl *M* saturée d'hydrogène. Coefficient angulaire: 33 mV/unité de log.

La courbe de polarisation correspondante a pour équation:

$$E = B + \frac{0.059}{2} \log \frac{(i - i_{H^+})^2}{(i_{H_2} - i)}$$

Lorsque la concentration des ions H^+ en solution est importante, i est négligeable devant i_{H^+} et:

$$E = B - 0.059 \text{ pH} - \frac{0.059}{2} \log (i_{H_2} - i)$$

La courbe représentative des variations de E en fonction de $\log (i_{H_2} - i)$ pour une solution d'acide chlorhydrique 0.1 *M*, est une droite de coefficient angulaire —34 mV/unité de log (Fig. 9) (valeur théorique —30 mV/unité de log).

c. Dans le cas d'une *solution alcaline*, la réaction oxydo-réductrice à considérer est:

$$H_2 + 2\,OH^- \rightleftarrows 2\,H_2O + 2e \quad \dots\dots\dots\dots\dots\dots \quad (2)$$

L'intensité anodique est limitée soit par la diffusion de H_2, soit par celle de OH^- si la solution est suffisamment peu concentrée en OH^-. Dans ce dernier cas, la courbe de polarisation anodique se compose de deux vagues: une première vague dont la hauteur est proportionnelle à la concentration des ions OH^- en solution, correspond à la réaction (1) et une seconde dont la hauteur est proportionnelle à la concentration de l'hydrogène dissous en solution, correspond à la réaction (2) et démarre au même potentiel que la vague d'oxydation de l'hydrogène en milieu neutre (courbe 4 de la Fig. 6).

La courbe de polarisation correspondant à la réaction (2) a pour équation:

$$E = A - \frac{0.059}{2} \log (i_{OH^-} - i)^2 (i_{H_2} - i)$$

Lorsque la concentration des ions OH^- en solution est importante, i est négligeable devant i_{OH^-} et:

$$E = A - 0.059 \text{ pH} - \frac{0.059}{2} \log (i_{H_2} - i)$$

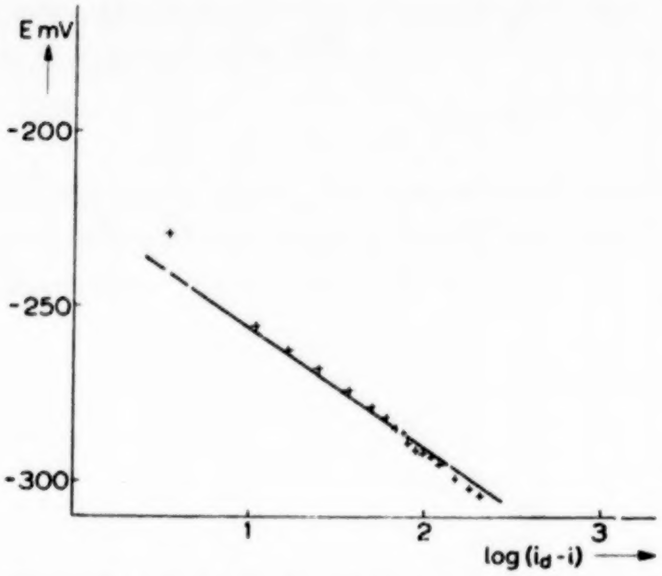

Fig. 9. Oxydo-réduction d'une solution HCl env. 0.1 *M*, NaCl *M* saturée d'hydrogène. Coefficient angulaire: —34 mV/unité de log.

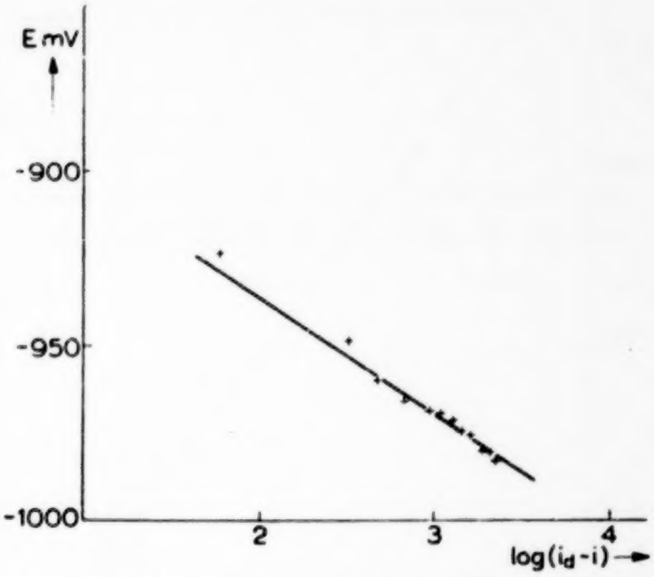

Fig. 10. Oxydo-réduction d'une solution NaOH env. 0.1 *M*, NaCl *M* saturée d'hydrogène. Coefficient angulaire —34 mV/unité de log.

La courbe représentative des variations de *E* en fonction de log ($i_{H_2} - i$) pour une solution d'hydroxyde de sodium 0.1 *M* est une droite de coefficient angulaire —34 mV/unité de log (Fig. 10) (valeur théorique —30 mV/unité de log).

Remarque: Ces résultats permettent d'envisager un dosage polarographique de l'hydrogène dissous en présence d'une électrode de platine platiné. Cette méthode pourrait convenir à la détermination de la teneur en hydrogène d'un mélange gazeux après saturation par celui-ci d'une solution acide ou alcaline.

Mesure du pH avec une électrode à hydrogène

La considération du faisceau de courbes de la Fig. 6 permet de prévoir les limites de fonctionnement de l'électrode à hydrogène. En effet, il est logique de supposer que, comme nos expériences le confirment, le potentiel d'équilibre à courant nul est d'autant plus rapidement atteint que les intensités anodique et cathodique correspondant à ce potentiel sont plus élevées. Au point de vue graphique, ceci se traduit par une intersection plus ou moins bien définie des courbes de polarisation avec la droite des courants nuls.

En milieu acide, lorsque la concentration des ions H^+ en solution varie, la hauteur du palier de diffusion cathodique correspondant à la réduction de H^+ reste proportionnelle à la concentration des ions H^+. Pour une concentration d'acide fort inférieure à 0.00005 *M*, l'intensité du courant de diffusion est de l'ordre de grandeur du courant résiduel et le potentiel d'équilibre de l'électrode à hydrogène est mal défini et non reproductible.

Parallèlement, en milieu alcalin, la hauteur du premier palier de diffusion anodique correspondant à l'oxydation de H_2 reste proportionnelle à la concentration des ions OH^-. Pour une concentration de base forte inférieure à 0.0001 *M*, l'intensité du courant de diffusion est de l'ordre de grandeur du courant résiduel et la mesure d'un potentiel d'équilibre dans ces conditions n'a pas grande signification.

Ce n'est qu'en milieu suffisamment tamponné que l'électrode à hydrogène peut fonctionner correctement.

Bibliographie p. 591

RÉSUMÉ

Les courbes de polarisation de l'eau et de ses ions en présence de platine platiné peuvent s'interpréter en admettant l'existence de deux réactions électrochimiques distinctes:

$$(1) \quad 2\,H^+ + 2e \rightleftarrows H_2$$
$$(2) \quad 2\,H_2O + 2e \rightleftarrows H_2 + 2\,OH^-$$

H_2O se comportant comme un complexe de H^+.

Nos résultats expérimentaux sont en accord avec les hypothèses suivantes utilisées pour obtenir les équations des courbes de polarisation: (a) les systèmes oxydo-réducteurs (1) et (2) sont rapides en présence de platine platiné.

(b) les vitesses de dissociation et de recombinaison de l'eau sont très grandes devant les vitesses de réaction électrochimique.

(c) les lois de l'équilibre chimique sont valables au voisinage de l'électrode.

Par ailleurs, nos résultats mettent en évidence les limites de fonctionnement de l'électrode à hydrogène.

SUMMARY

The polarization curves of water and its ions in the presence of platinized platinum can be interpreted as conceding the existence of two distinct electrochemical reactions:

$$(1) \quad 2\,H^+ + 2e \rightleftarrows H_2$$
$$(2) \quad 2\,H_2O + 2e \rightleftarrows H_2 + 2\,OH^-$$

H_2O acting as a H^+ complex.

Our experimental results are in agreement with the following hypotheses used to obtain the equations of the polarization curves:

(a) the oxidation-reduction systems (1) and (2) are rapid in the presence of platinized platinum;

(b) the dissociation and recombination speeds of water are very great compared with the speeds of the electrochemical reaction;

(c) the laws of chemical equilibrium are valid in the vicinity of the electrode.

Our results demonstrate the functional limits of the hydrogen electrode.

ZUSAMMENFASSUNG

Die Polarisationskurven des Wassers und seiner Ionen in Gegenwart von platiniertem Platin können mit Hilfe der Annahme der folgenden zwei selbstständigen elektrochemischen Reaktionen interpretiert werden:

$$(1) \quad 2\,H^+ + 2e \rightleftarrows H_2$$
$$(2) \quad 2\,H_2O + 2e \rightleftarrows H_2 + 2\,OH^-$$

wobei sich H_2O wie ein Komplex von H^+ verhält.

Unsere Versuchsergebnisse sind in Übereinstimmung mit den folgenden Hypothesen, welche zur Aufstellung der Gleichungen der Polarisationskurven benutzt wurden:

(a) Die Oxydoreduktionssysteme (1) und (2) sind schnell in Gegenwart von platiniertem Platin.

(b) Die Dissoziations- und Wiederverbindungs-Geschwindigkeiten des Wassers sind sehr gross im Verhältnis zu den Geschwindigkeiten elektrochemischer Reaktionen.

(c) Die Gesetze des chemischen Gleichgewichtes gelten in der Nähe der Elektrode.

Unsere Versuchsergebnisse zeigen die Grenzen an, innerhalb derer die Wasserstoffelektrode funktioniert.

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DOSAGE POLAROGRAPHIQUE DU GERMANIUM DANS DES MINERAIS ET CONCENTRÉS GERMANIFÈRES

par

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INTRODUCTION

Les méthodes de dosage du germanium décrites dans la littérature sont généralement précédées d'une séparation de $GeCl_4$ par distillation.

Nous nous sommes proposés de mettre au point une méthode très générale de dosage du germanium dans des matières germanifères complexes et variées en combinant l'extraction au tétrachlorure de carbone[1,2] et la polarographie.

I. MISE AU POINT DE LA MÉTHODE

1. Dosage polarographique du germanium

Dans une publication antérieure[3], nous avons exposé les résultats d'une étude de la réduction polarographique du germanium tétravalent. Signalons toutefois deux particularités de ce travail: tout d'abord, tous les essais ont été faits au polarographe Blomgren LKB en raison de sa plus grande sensibilité; ensuite, nous ne sommes parvenus pour les solutions diluées à doser le germanium avec une précision suffisante qu'en déterminant de manière séparée la courbe du courant résiduel. De cette façon, on arrive, même pour des solutions $10^{-5}M$ en Ge à une précision de l'ordre de 1.3%.

2. Étude de l'extraction du germanium au tétrachlorure de carbone

a) Influence de la concentration en HCl sur le taux d'extraction. Les essais ont été réalisés en équilibrant 40 ml de solution chlorhydrique $6.31 \cdot 10^{-4}M$ en Ge avec 40 ml de CCl_4. Après séparation des deux phases, le germanium extrait par CCl_4 est transféré à nouveau dans l'eau par agitation et dosé par polarographie. Les résultats sont représentés par la Fig. 1 donnant le pourcentage d'extraction P en fonction de la normalité en HCl. Celle-ci montre que l'extraction est complète lorsque la normalité en HCl est au moins égale à 8 (pour des volumes égaux des deux phases).

b) Influence de la concentration en germanium. En principe, le germanium peut se trouver dans la solution aqueuse sous différentes formes moléculaires et dans ces conditions il est possible que le coefficient de partage varie avec la quantité de germanium. Dans ce but, nous avons fait une série d'essais de partage en équilibrant 100 ml de solution aqueuse HCl 8N contenant des quantités croissantes de germanium avec 10 ml CCl_4. Dès que l'équilibre est atteint, on sépare les deux phases et on y dose le germanium. Le Tableau I résume les résultats obtenus.

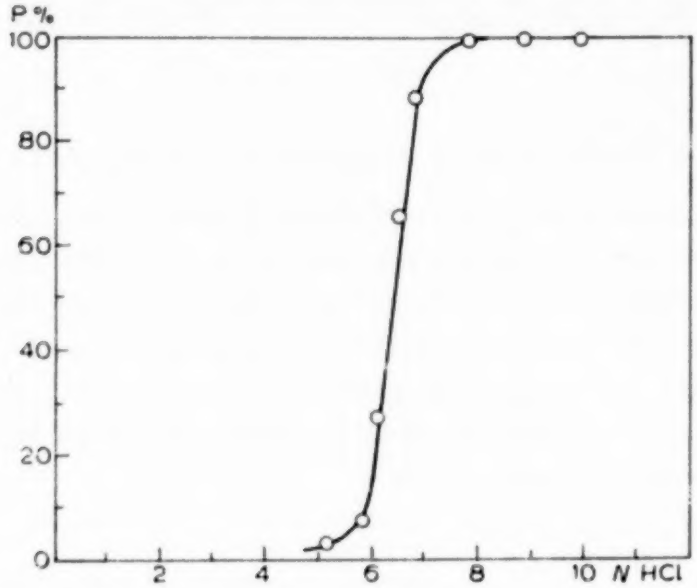

Fig. 1. Courbe du pourcentage d'extraction du germanium en fonction de la normalité en HCl.

TABLEAU I

CONDITIONS D'EXTRACTION: HCl 8N: VOLUME PHASE AQUEUSE: 100 ml
VOLUME PHASE ORGANIQUE: 10 ml

Concentration initiale en Ge en mole/litre	*Pourcent d'extraction P*	*Coefficient de partage α*	*Moyen α*
$5.85 \cdot 10^{-3}$	81.2	43	45.7
$5.81 \cdot 10^{-3}$	82.5	47	
$5.81 \cdot 10^{-3}$	82.5	47	
$2.66 \cdot 10^{-3}$	91.7	110	
$2.65 \cdot 10^{-3}$	92.4	122	116
$2.65 \cdot 10^{-3}$	92.1	116	
$2.68 \cdot 10^{-3}$	92.0	115	
$6.35 \cdot 10^{-4}$	91.1	102	
$6.37 \cdot 10^{-4}$	91.7	110	104
$6.40 \cdot 10^{-4}$	91.6	108	
$6.37 \cdot 10^{-4}$	90.7	98	
$6.61 \cdot 10^{-5}$	93.0	133	
$6.61 \cdot 10^{-5}$	91.0	101	122
$6.61 \cdot 10^{-5}$	92.5	123	
$6.57 \cdot 10^{-5}$	93.0	133	

On voit que, pour des concentrations initiales en Ge dans l'eau de 2.10^{-5} à $6.10^{-5} M$, le coefficient de partage est de l'ordre de 114 ± 8. Toutefois, pour des concentrations en

Bibliographie p. 596

Ge supérieures à $2.6 \cdot 10^{-3} M$ on observe une diminution très importante du coefficient de partage. En pratique, nous nous placerons pour les dosages dans la zone de concentration où le coefficient de partage est constant.

c) Recherche des conditions pratiques pour l'extraction. Nous avons pu etablir que, dans le cas qui nous intéresse, une double extraction avec 40 ml de CCl_4 rend l'extraction complète. Des essais sur des solutions synthétiques dans un domaine de concentration en germanium allant de $2.50 \cdot 10^{-4}$ jusqu'à $3.12 \cdot 10^{-6} M$ ont donné des résultats satisfaisants.

II. APPLICATION DE LA MÉTHODE D'ANALYSE À DES PRODUITS GERMANIFÈRES

Nous avons eu l'occasion d'essayer la méthode d'analyse dont nous allons donner les détails du mode opératoire, sur une grande variété de produits germanifères (minerais, concentrés, résidus de différentes espèces, charbons, poussières, etc.) et la concordance des résultats obtenus avec ceux des méthodes colorimétriques ou spectroscopiques indique que la méthode que nous proposons est non seulement exacte et précise mais qu'elle est d'application très générale tant au point de vue de la nature du produit à analyser que de sa teneur en germanium.

a. Attaque

Suivant la teneur présumée en germanium, attaquer 0.2 à 0.5 g pour les matières riches et 1 à 2.5 g pour les matières pauvres, par une fusion au peroxyde de sodium (1 à 2 g) granulé fin dans un creuset en alsint OB.

Reprendre la masse de la fusion par 30 ml d'eau et l'introduire dans un ballon de 500 ml pour les fortes teneurs et dans un ballon de 100 ml pour les faibles teneurs. La dissolution des oxydes est obtenue par addition de 10 à 20 ml d'HCl $12N$ refroidi préalablement à la température de la glace pour éviter les pertes en germanium par volatilisation du $GeCl_4$.

Compléter au volume avec de l'eau distillée.

b. Extraction et préparation de la solution à polarographier

Prélever suivant la teneur en germanium de l'échantillon 10 à 35 ml de solution et l'introduire dans l'ampoule à extraction contenant 40 ml de CCl_4. On aura soin au préalable de détruire le chlore et les hypochlorites de la solution par introduction d'une quantité de chlorhydrate d'hydroxylamine à froid, jusqu'à ce qu'on ne perçoive plus l'odeur de chlore.

Rendre ensuite la solution, déjà légèrement acide, $8N$ en HCl, par addition d'une quantité calculée d'HCl $12N$ (refroidi préalablement à la température de la glace) et agiter l'ampoule pendant 2 minutes. Renouveler l'extraction par 40 ml de CCl_4. Dans le cas où il apparaît un précipité de chlorure de sodium dans l'ampoule, effectuer une troisième extraction par 15 ml de CCl_4 et un certain volume d'eau servant à la dissolution du sel. Cette précaution est prise en vue de récupérer des faibles fractions de germanium éventuellement enrobées dans le chlorure de sodium. Les fractions organiques réunies sont agitées pendant 1 à 2 minutes par 5 à 8 ml d'HCl $10N$ en vue d'éliminer les gouttes de solution aqueuse entraînées. La phase organique est enfin agitée pendant 2 minutes avec deux fois 10 ml d'eau.

Laver les ampoules par 12 ml de la solution tampon H_3BO_3 $0.1M$ + NaOH $0.1N$ à pH = 8.9 et ajouter ce liquide à la solution aqueuse préalablement additionnée de 2.5 ml de KCl $1M$ et de 1 ml de gélatine à 0.5%; ajuster le pH entre 8.8 et 9.0 et compléter la solution dans un ballon de 50 ml.

Introduire 20 ml de cette solution dans la cellule. Dégazer pendant 20 à 30 minutes par un courant d'azote pur et passer au polarographe. Ajouter ensuite 5 ml d'une solution de germanium titrée et enregistrer à nouveau. Corriger les deux polarogrammes du courant résiduel obtenu par un enregistrement de l'électrolyte effectué dans les mêmes conditions.

RÉSULTATS

Nous donnons dans le Tableau II, les résultats obtenus par cette méthode sur une quinzaine de matières de composition complexe et de nature très variée.

Bibliographie p. 596

La deuxième colonne donne, pour un même échantillon, les différents résultats obtenus.

La troisième colonne donne le résultat de l'analyse obtenu par une autre méthode ou par un laboratoire étranger.

TABLEAU II

Échantillon no.	*Ge trouvé par polarographie %*	*Ge obtenu par une autre méthode %*
1	20.0 ; 20.0 ; 20.2 ; 19.9	20.0
2	12.8 ; 12.8 ; 12.9 13.1	12.8_5
3	2.79 ; 2.81 ; 2.70 2.73 2.75 ; 2.70 ; 2.78 ; 2.77 2.77 ; 2.83	2.64
4	0.324 ; 0.331 ; 0.334 ; 0.334	0.345
5	0.244 ; 0.244 ; 0.247	0.230
6	0.147 ; 0.145 ; 0.144 ; 0.145	0.146
7	0.051_7; 0.053_4; 0.050_8; 0.051_7	0.054
8	0.030_4; 0.030_6; 0.030_1	0.027
9	0.029 ; 0.028_5	0.025
10	0.020_9 0.021_4; 0.021_4; 0.020_9	0.018
11	0.018_4; 0.019_1; 0.017_7	0.019
12	0.006_8; 0.006_8; 0.006_8	0.006
13	0.006_4; 0.006_4; 0.006_2; 0.006_9	—
14	0.006_2; 0.006_4; 0.006_4	0.006_5
Résidus de charbons belges*		
1	0.001_7; 0.001_7	0.001_8
2	0.002_8	0.002_5
3	0.001_4; 0.001_5	—

* *Remarque pour les charbons.* Étant donné la très faible teneur en germanium dans les charbons (de l'ordre de 1 à 2 p.p.m.), on commence par une incinération en le chauffant dans un four réglé à 450°C jusqu'à poids constant. On prélève 1 g de cendre, on effectue une fusion et on introduit la solution dans un ballon de 50 ml.

CONCLUSION

La méthode proposée, combinant l'extraction et la polarographie après mise en solution par fusion au peroxyde, est plus rapide que celle basée sur la distillation; elle permet de doser directement le germanium aussi bien dans des produits riches (concentrés jusqu'à 20%) que dans des minerais très pauvres (0.0005%) avec une précision de l'ordre de 1 à 2%. L'erreur du dosage est pratiquement celle de la mesure polarographique.

RÉSUMÉ

Les auteurs exposent une méthode d'analyse du germanium combinant la séparation par extraction du $GeCl_4$ au CCl_4 et le dosage polarographique du Ge^{IV}. Après une étude systématique du coefficient de partage du germanium entre le tétrachlorure de carbone et une solution aqueuse, en fonction de la normalité en acide chlorhydrique et de la quantité de germanium, les conditions de l'extraction en vue d'obtenir une séparation quantitative sont précisées.

La méthode a été expérimentée sur une série de matières germanifères de nature très complexe dont la teneur en germanium varie depuis le millième jusqu'à quelques dizaines de pourcent. Les résultats sont obtenus avec une précision variant entre 0.5 et 2%.

Bibliographie p. 596

SUMMARY

The authors describe a method for the analysis of germanium combining the extraction of $GeCl_4$ by CCl_4 and the polarographic determination of Ge^{IV}. After a systematic study of the distribution coefficient of germanium between carbon tetrachloride and an aqueous solution versus the normality in hydrochloric acid and the quantity of germanium, the conditions of extraction in view to obtain quantitative separation are determined. The method has been tried on a great variety of germanium samples of complex kind in which the content of germanium varies from 0.001 to some ten percent. The results obtained are reproducible within 0.5 to 2.0%.

ZUSAMMENFASSUNG

Die Verfasser legen zur Analyse des Germaniums eine Methode dar, welche die Trennung durch Extraktion des $GeCl_4$ mit CCl_4 und die polarographische Bestimmung des Ge^{IV} umfasst.

Nach einer planmässigen Untersuchung des Verteilungskoeffizienten des Germaniums zwischen Tetrachlorkohlenstoff und einer wässrigen Lösung in Abhängigkeit von der Normalität der Salzsäure und der Germanium-Menge werden die Extraktionsbedingungen welcher zu quantitativer Trennung führen, angegeben.

Diese Methode wurde an einer Reihe germaniumhältiger Stoffe von mannigfaltiger Art deren Gehalt an Germanium zwischen 0.001 und etwa 10 Prozent schwankte, ausprobiert.

Die Ergebnisse sind innerhalb von 0.5 bis 2.0% reproduzierbar.

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